

7057-001-95X

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF:

KRZYSZTOF MATYJASZEWSKI ET AL : EXAMINER: CHENG

SERIAL NO. 08/414,415

FILED: MARCH 31, 1995 : GROUP ART UNIT: 1505

FOR: NOVEL (CO)POLYMERS AND A NOVEL  
POLYMERIZATION PROCESS BASED ON  
ATOM (OR GROUP) TRANSFER RADICAL  
POLYMERIZATION

DECLARATION UNDER 37 C.F.R. §1.132

ASSISTANT COMMISSIONER FOR PATENTS  
WASHINGTON, D.C. 20231

SIR:

Now comes KRZYSZTOF MATYJASZEWSKI who deposes and says that:

1. I am one of the joint inventors of the above-identified application.
2. I graduated from Polish Academy of Sain '76, receiving my Ph.D degree in Chemistry and have been employed since '85 by Ceramique Hellier Clerc, and engaged in education and research.
3. Under my supervision and control the following experiments were carried out in order to show support for the breadth of the claims in the above-identified application. These experiments provide evidence for the use of a wide range of metals, ligands, and monomers in the presently claimed process and production of a wide variety of polymer types.

The various metals and ligands shown in these examples include various of the preferred embodiments disclosed in the present specification, as well as various embodiments

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included within the present claims that were not preferred embodiments in the present application, but have since been found to also work in the present process.

### **Example 1**

**Bulk Polymerization using  $\text{FeBr}_2$  / dNBipy:** The following reagents were transferred into glass tubes purged with argon: 19.0 mg ( $8.73 \times 10^{-2}$  mmol) of  $\text{FeBr}_2$ , 1.0 ml (8.73 mmol) of styrene, 12.0 ml ( $8.73 \times 10^{-2}$  mmol) of 1-phenylethyl bromide and 71.2 mg ( $17.5 \times 10^{-2}$  mmol) of 4,4'-di(5-nonyl)-2,2'-bipyridine. Each tube was degassed three times by "freeze-pump-thaw" cycles and sealed under vacuum. The tubes were placed in an oil bath thermostated at 110 °C and were removed from the oil bath at timed intervals.

<b>Sample</b>	<b>Time(hr)</b>	<b>Conv. (%)</b>	<b><math>M_n</math> (th.)</b>	<b><math>M_n</math> (GPC)</b>	<b><math>M_w / M_n</math></b>
1	3.0	13.9	1,400	1,600	1.25
2	6.8	26.3	2,700	2,700	1.20
3	12.0	37.8	3,900	4,200	1.16
4	21.0	64.0	6,700	6,500	1.27

### **MMA**

### **Example 2**

**Solution Polymerization with  $\text{FeBr}_2$  / 4,4'-di(5-nonyl)-2,2'-bipyridine / p-toluenesulfonyl chloride:** 62.5 mg (0.29 mmol)  $\text{FeBr}_2$ , 4.5 ml(42.1 mmol) methyl methacrylate , 118.3 mg (0.29 mmol) 4,4'-di(5-nonyl)-2,2'-bipyridine, and 4.0 ml p-xylene were added to a dry round-bottomed flask under an argon atmosphere. 55.3 mg (0.29 mmol) p-toluenesulfonyl chloride in 0.5 ml methyl methacrylate was added to the flask which was then immersed in an oil bath thermostated

at 90 °C. A positive argon pressure was maintained throughout the reaction and samples were withdrawn at timed intervals.

<b>Sample</b>	<b>Time (h)</b>	<b>Conversion (%)</b>	<b>M<sub>n</sub>, Cal</b>	<b>M<sub>n</sub>, SEC</b>	<b>M<sub>w</sub> / M<sub>n</sub></b>
1	0.75	21.2	3,400	5,400	1.27
2	1.8	43.6	7,100	9,400	1.25
3	3.2	67.5	11,000	13,100	1.25
4	4.21	77.1	12,500	15,100	1.25
5	5.3	84.4	13,700	16,300	1.25
6	6.3	87.7	14,200	15,700	1.29

### **Example 3**

**Solution Polymerization with FeBr<sub>2</sub> / 4,4'-di(5-nonyl)-2,2'-bipyridine / methansulfonyl chloride:** 62.5 mg (0.29 mmol) FeBr<sub>2</sub>, 4.5 ml (42.1 mmol) methyl methacrylate, 118.3 mg (0.29 mmol) 4,4'-di(5-nonyl)-2,2'-bipyridine, and 4.0 ml p-xylene were added to a dry round-bottomed flask under an argon atmosphere. 33.2 mg (0.29 mmol) methanesulfonyl chloride in 0.5 ml methyl methacrylate was added to the flask which was then immersed in an oil bath thermostated at 90 °C. A positive argon pressure was maintained throughout the reaction and samples were withdrawn at timed intervals.

<b>Sample</b>	<b>Time (h)</b>	<b>Conversion (%)</b>	<b>M<sub>n</sub>, Cal</b>	<b>M<sub>n</sub>, SEC</b>	<b>M<sub>w</sub> / M<sub>n</sub></b>
1	0.8	25.0	4,000	5,200	1.31

2	1.8	41.0	6,600	8,400	1.25
3	3.2	57.6	9,300	11,100	1.24
4	4.2	66.9	10,800	11,800	1.25
5	5.3	73.4	11,900	13,500	1.24
6	6.3	76.8	12,400	13,600	1.25
7	8.5	81.9	13,300	13,600	1.31

#### Example 4

**Solution Polymerization with  $\text{FeBr}_2$  / 4,4'-di(5-nonyl)-2,2'-bipyridine / ethyl 2 -bromo isobutyrate:** 62.5 mg (0.29 mmol)  $\text{FeBr}_2$ , 4.5 ml (42.1 mmol) methyl methacrylate , 118.3 mg (0.29 mmol) 4,4'-di(5-nonyl)-2,2'-bipyridine, and 4.0 ml p-xylene were added to a dry round-bottomed flask under an argon atmosphere. 42.6  $\mu\text{l}$  (0.29 mmol) ethyl 2-bromo isobutyrate in 0.5 ml methyl methacrylate was added to the flask which was then immersed in an oil bath thermostated at 90 °C. A positive argon pressure was maintained throughout the reaction and samples were withdrawn at timed intervals.

Sample	Time (h)	Conversion (%)	$M_n$ , Cal	$M_n$ , SEC	$M_w/M_n$
1	0.3	24.0	3,900	7,500	1.39
2	0.9	45.4	7,300	10,200	1.34
3	1.2	56.8	9,200	11,100	1.34
4	1.8	68.5	11,100	11,900	1.33
5	2.7	80.0	13,000	14,100	1.31
6	3.5	85.6	13,900	13,300	1.32
7	4.2	87.3	14,100	13,600	1.35
8	4.3	89.0	14,400	13,600	1.34

### Example 5

**Solution Polymerization with  $\text{FeBr}_2$  / 4,4'-di(5-nonyl)-2,2'-bipyridine / 2 - bromopropionitrile:** 62.5 mg (0.29 mmol)  $\text{FeBr}_2$ , 4.5 ml(42.1 mmol) methyl methacrylate , 118.3 mg (0.29 mmol) 4,4'-di(5-nonyl)-2,2'-bipyridine, and 4.0 ml p-xylene were added to a dry round-bottomed flask under an argon atmosphere. 25.1  $\mu\text{l}$  (0.29 mmol) 2-bromopropionitrile in 0.5 ml methyl methacrylate was added to the flask which was then immersed in an oil bath thermostated at 90 °C. A positive argon pressure was maintained throughout the reaction and samples were withdrawn at timed intervals.

<b>Sample</b>	<b>Time (h)</b>	<b>Conversion (%)</b>	<b><math>M_n</math>, Cal</b>	<b><math>M_n</math>, SEC</b>	<b><math>M_w/M_n</math></b>
1	0.3	21.1	3,40	5,000	1.38
2	0.9	39.6	6,400	7,700	1.25
3	1.2	48.6	7,800	8,900	1.23
4	1.9	61.5	9,900	10,500	1.20
5	2.7	73.1	11,800	11,600	1.20
6	3.5	80.3	13,000	12,600	1.21
7	4.3	86.2	13,900	12,700	1.23
8	6.0	91.0	14,700	12,600	1.28

### Example 6

**Solution Polymerization with  $\text{FeBr}_2$  / 4,4'-di(5-nonyl)-2,2'-bipyridine / methyl a - bromophenylacetate:** 62.5 mg (0.29 mmol)  $\text{FeBr}_2$ , 4.5 ml(42.1 mmol) methyl methacrylate , 118.3 mg (0.29 mmol) 4,4'-di(5-nonyl)-2,2'-bipyridine, and 4.0 ml p-xylene were added to a dry round-bottomed flask under an argon atmosphere. 66.4 mg (0.29 mmol) methyl -

bromophenylacetate in 0.5 ml methyl methacrylate was added to the flask which was then immersed in an oil bath thermostated at 90 °C. A positive argon pressure was maintained throughout the reaction and samples were withdrawn at timed intervals.

<b>Sample</b>	<b>Time (h)</b>	<b>Conversion (%)</b>	<b>M<sub>n</sub>, Cal</b>	<b>M<sub>n</sub>, SEC</b>	<b>M<sub>w</sub> / M<sub>n</sub></b>
1	0.3	4.5	700	1,000	1.28
2	0.7	8.2	1,300	1,200	1.26
3	1.2	11.3	1,800	1,700	1.25
4	1.8	17.3	2,800	2,400	1.21
5	2.6	24.5	4,000	3,300	1.18
6	4.0	35.2	5,700	5,500	1.14
7	8.5	61.8	10,000	8,100	1.16
8	10.8	70.6	11,400	8,500	1.19
9	18.3	75.2	12,200	9,000	1.27

### Example 7

**Solution Polymerization with FeBr<sub>2</sub> / 4,4'-di(5-nonyl)-2,2'-bipyridine / bromodiphenylmethane:** 62.5 mg (0.29 mmol) FeBr<sub>2</sub>, 4.5 ml (42.1 mmol) methyl methacrylate, 118.3 mg (0.29 mmol) 4,4'-di(5-nonyl)-2,2'-bipyridine, and 4.0 ml p-xylene were added to a dry round-bottomed flask under an argon atmosphere. 71.7 mg (0.29 mmol) bromodiphenylmethane in 0.5 ml methyl methacrylate was added to the flask which was then immersed in an oil bath thermostated at 90 °C. A positive argon pressure was maintained throughout the reaction and samples were withdrawn at timed intervals.

<u>Sample</u>	<u>Time (h)</u>	<u>Conversion (%)</u>	<u>M<sub>n</sub>, Cal</u>	<u>M<sub>n</sub>, SEC</u>	<u>M<sub>w</sub>/M<sub>n</sub></u>
1	1.0	8.5	1,400	2,500	1.21
2	3.7	33.8	5,500	8,900	1.09
3	5.8	47.3	7,600	12,400	1.11
4	8.1	57.4	9,300	14,500	1.15
5	10.0	64.7	10,500	15,500	1.18
6	12.0	69.7	11,300	16,600	1.19

**Manganese (II) X<sub>2</sub>**

**Styrene**

**Example 8**

**Heterogeneous ATRP of styrene using MnCl<sub>2</sub> as catalyst:** The following amounts of reagents were weighed into a glass tube under ambient temperature: 12mg ( $8.15 \times 10^{-2}$  mmol) of MnCl<sub>2</sub>, 1.00 mL (0.909 g, 8.73 mmol) of deinhibited styrene, 28 mg (0.175 mmol) 2,2'-bipyridine, and 10 mL ( $8.8 \times 10^{-2}$  mmol) 1-phenylethyl chloride. Two “freeze-pump-thaw” cycles were performed on the contents of the tube to ensure that oxygen was removed from the polymerization solution. The tube was sealed under vacuum then placed in an oil bath thermostated at 90 °C. After 7 h the tube was broken, and the contents were dissolved in 10 mL of THF. Conversion of the monomer, measured using GC was 71 %, and the molecular weight and polydispersity measured by GPC were M<sub>n</sub> = 7,300, and M<sub>w</sub>/M<sub>n</sub> = 1.55.

### **Example 9**

**Homogeneous ATRP of styrene using MnCl<sub>2</sub> as catalyst:** The following amounts of reagents were weighed into a glass tube under ambient temperature: 12mg (8.15x10<sup>-2</sup> mmol) of MnCl<sub>2</sub>, 1.00 mL (0.909 g, 8.73 mmol) of deinhibited styrene, 60 mg (0.175 mmol) 4,4'-di-(5-nonyl)-2,2'-bipyridine, and 10 mL (8.8x10<sup>-2</sup> mmol) 1-phenylethyl chloride. Two “freeze-pump-thaw” cycles were performed on the contents of the tube in order to insure that oxygen was removed from the polymerization solution. The tube was sealed under vacuum, then placed in an oil bath thermostated at 90 °C. After 12 h the tube was broken, and the contents were dissolved in 10 mL of THF. Conversion of the monomer, measured using GC was 85 %, and the molecular weight and polydispersity measured by GPC were M<sub>n</sub> = 8,300, and M<sub>w</sub>/M<sub>n</sub> = 1.45.

### **Methyl Acrylate**

### **Example 10**

**Heterogeneous ATRP of methyl acrylate using MnCl<sub>2</sub> as catalyst:** The following amounts of reagents were weighed into a glass tube under ambient temperature: 12mg (8.15x10<sup>-2</sup> mmol) of MnCl<sub>2</sub>, 1.00 mL (0.956 g, 8.88 mmol) of deinhibited methyl acrylate, 28 mg (0.175 mmol) 2,2'-bipyridine, and 11 mL (8.8x10<sup>-2</sup> mmol) methyl 2-chloropropionate. Two “freeze-pump-thaw” cycles were performed on the contents of tube to insure that oxygen was removed from the polymerization solution. The tube was sealed under vacuum then placed in an oil bath thermostated at 90 °C. After 7 h the tube was broken, and the contents were dissolved in 10 mL of THF. Conversion of the monomer, measured using GC was 81 %, and the molecular weight and polydispersity measured by GPC were M<sub>n</sub> = 8,100, and M<sub>w</sub>/M<sub>n</sub> = 2.01.

### **Example 11**

**Homogeneous ATRP of methyl acrylate using  $MnCl_2$  as catalyst:** The following amounts of reagents were weighed into a glass tube under ambient temperature: 12mg ( $8.15 \times 10^{-2}$  mmol) of  $MnCl_2$ , 1.00 mL (0.956 g, 8.88 mmol) of deinhibited methyl acrylate, 60 mg (0.175 mmol) 4,4'-di-(5-nonyl)-2,2'-bipyridine, and 11 mL ( $8.8 \times 10^{-2}$  mmol) methyl 2-chloropropionate. Two "freeze-pump-thaw" cycles were performed on the contents of the tube in order to insure that oxygen was removed from the polymerization solution. The tube was sealed under vacuum, then placed in an oil bath thermostated at 90 °C. After 12 h the tube was broken, and the contents were dissolved in 10 mL of THF. Conversion of the monomer, measured using GC was 98 %, and the molecular weight and polydispersity measured by GPC were  $M_n = 10,600$ , and  $M_w/M_n = 1.95$ .

### **Methyl Methacrylate**

### **Example 12**

**Heterogeneous ATRP of methyl methacrylate using  $MnCl_2$  as catalyst:** The following amounts of reagents were weighed into a glass tube under ambient temperature: 12mg ( $8.15 \times 10^{-2}$  mmol) of  $MnCl_2$ , 1.00 mL (0.936 g, 8.87 mmol) of deinhibited methyl acrylate, 28 mg (0.175 mmol) 2,2'-bipyridine, and 19 mg ( $8.8 \times 10^{-2}$  mmol) toluenesulfonyl chloride. Two "freeze-pump-thaw" cycles were performed on the contents of tube to insure that oxygen was removed from the polymerization solution. The tube was sealed under vacuum then placed in an oil bath thermostated at 90 °C. After 7 h the tube was broken, and the contents were dissolved in 10 mL of THF. Percent conversion of the sample, measured using GC was 84 %, and the molecular weight and polydispersity measured by GPC were  $M_n = 8,600$ , and  $M_w/M_n = 1.67$ .

### **Example 13**

**Homogeneous ATRP of methyl methacrylate using MnCl<sub>2</sub> as catalyst:** The following amounts of reagents were weighed into a glass tube under ambient temperature: 12mg ( $8.15 \times 10^{-2}$  mmol) of MnCl<sub>2</sub>, 1.00 mL (0.936 g, 8.87 mmol) of deinhibited methyl acrylate, 60 mg (0.175 mmol) 4,4'-di-(5-nonyl)-2,2'-bipyridine, and 19 mg ( $8.8 \times 10^{-2}$  mmol) toluenesulfonyl chloride. Two “freeze-pump-thaw” cycles were performed on the contents of the tube in order to insure that oxygen was removed from the polymerization solution. The tube was sealed under vacuum then placed in an oil bath thermostated at 90 °C. After 12 h the tube was broken, and the contents were dissolved in 10 mL of THF. Percent conversion of the sample, measured using GC was 98 %, and the molecular weight and polydispersity measured by GPC were M<sub>n</sub> = 9,900, and M<sub>w</sub>/M<sub>n</sub> = 1.57.

### **CrCl<sub>2</sub> Catalysts**

### **Example 14**

**Homogeneous ATRP of styrene using CrCl<sub>2</sub> as catalyst:** The following amounts of reagents were weighed into a glass tube under ambient temperature: 12mg ( $8.37 \times 10^{-2}$  mmol) of CrCl<sub>2</sub>, 1.00 mL (0.909 g, 8.73 mmol) of deinhibited styrene, 60 mg (0.175 mmol) 4,4'-di-(5-nonyl)-2,2'-bipyridine, and 10 mL ( $8.8 \times 10^{-2}$  mmol) 1-phenylethyl chloride. Two “freeze-pump-thaw” cycles were performed on the content of the tube to insure that oxygen was removed from the polymerization solution. The tube was sealed under vacuum then placed in an oil bath thermostated at 90 °C. After 3 h the tube was broken, and the contents were dissolved in 10 mL

of THF. Conversion of the monomer, measured using GC was 98 %, and the molecular weight and polydispersity measured by GPC were  $M_n = 30,200$ , and  $M_w/M_n = 1.78$ .

### **Example 15**

**Homogeneous ATRP of methyl acrylate using  $\text{CrCl}_2$  as catalyst:** The following amounts of reagents were weighed into glass tube under ambient temperature: 12mg ( $8.37 \times 10^{-2}$  mmol) of  $\text{CrCl}_2$ , 1.00 mL (0.956 g, 8.88 mmol) of deinhibited methyl acrylate, 60 mg (0.175 mmol) 4,4'-di-(5-nonyl)-2,2'-bipyridine, and 11 mL ( $8.8 \times 10^{-2}$  mmol) methyl 2-chloropropionate. Two "freeze-pump-thaw" cycles were performed on the contents of the tube to insure that oxygen was removed from the polymerization solution. The tube was sealed under vacuum then placed in an oil bath thermostated at 90 °C. After 3 h the tube was broken, and the contents were dissolved in 10 mL of THF. Conversion of the monomer, measured using GC was 100 %, and the molecular weight and polydispersity measured by GPC were  $M_n = 41,6000$ , and  $M_w/M_n = 2.01$ .

### **Example 16**

**Homogeneous ATRP of methyl methacrylate using  $\text{CrCl}_2$  as catalyst:** The following amounts of reagents were weighed into a glass tube under ambient temperature: 12mg ( $8.37 \times 10^{-2}$  mmol) of  $\text{CrCl}_2$ , 1.00 mL (0.936 g, 8.87 mmol) of deinhibited methyl acrylate, 60 mg (0.175 mmol) 4,4'-di-(5-nonyl)-2,2'-bipyridine, and 19 mg ( $8.8 \times 10^{-2}$  mmol) toluenesulfonyl chloride. Two

“freeze-pump-thaw” cycles were performed on the contents of the tube to insure that oxygen was removed from the polymerization solution. The tube was sealed under vacuum then placed in an oil bath thermostated at 90 °C. After 3 h the tube was broken, and the contents were dissolved in 10 mL of THF. Conversion of the monomer, measured using GC was 99 %, and the molecular weight and polydispersity measured by GPC were  $M_n = 38,500$ , and  $M_w/M_n = 2.10$ .

### **MnCl<sub>2</sub> / CrCl<sub>3</sub> Co-Catalysts**

#### **Example 17**

**Homogeneous ATRP of styrene using MnCl<sub>2</sub>/CrCl<sub>3</sub> as catalyst:** The following amounts of reagents were weighed into a glass tube under ambient temperature: 12mg ( $8.15 \times 10^{-2}$  mmol) of MnCl<sub>2</sub>, 2mg ( $10^{-2}$  mmol) CrCl<sub>3</sub>, 1.00 mL (0.909 g, 8.73 mmol) of deinhibited styrene, 60 mg (0.175 mmol) 4,4'-di-(5-nonyl)-2,2'-bipyridine, and 10 mL ( $8.8 \times 10^{-2}$  mmol) phenylethyl chloride. Two “freeze-pump-thaw” cycles were performed on the contents of the tube in order to insure that oxygen was removed from the polymerization solution. The tube was sealed under vacuum then placed in an oil bath thermostated at 90 °C. After 7 h the tube was broken, and the contents were dissolved in 10 mL of THF. Conversion of the monomer, measured using GC was 82 %, and the molecular weight and polydispersity measured by GPC were  $M_n = 8,300$ , and  $M_w/M_n = 1.48$ .

#### **Example 18**

**Homogeneous ATRP of methyl acrylate using MnCl<sub>2</sub>/CrCl<sub>3</sub> as catalyst:** The following amounts of reagents were weighed into a glass tube under ambient temperature: 12mg ( $8.15 \times 10^{-2}$

mmol) of  $\text{MnCl}_2$ , 2mg ( $10^{-2}$  mmol)  $\text{CrCl}_3$ , 1.00 mL (0.956 g, 8.88 mmol) of deinhibited methyl acrylate, 60 mg (0.175 mmol) 4,4'-di-(5-nonyl)-2,2'-bipyridine, and 11 mL ( $8.8 \times 10^{-2}$  mmol) methyl 2-chloropropionate. Two "freeze-pump-thaw" cycles were performed on the contents of the tube in order to insure that oxygen was removed from the polymerization solution. The tube was sealed under vacuum then placed in an oil bath thermostated at 90 °C. After 7 h the tube was broken, and the contents were dissolved in 10 mL of THF. Conversion of the monomer, measured using GC was 97 %, and the molecular weight and polydispersity measured by GPC were  $M_n = 10,200$ , and  $M_w/M_n = 1.92$ .

### **Example 19**

**Homogeneous ATRP of methyl methacrylate using  $\text{MnCl}_2/\text{CrCl}_3$  as catalyst:** The following amounts of reagents were weighed into glass tube under ambient temperature: 12mg ( $8.15 \times 10^{-2}$  mmol) of  $\text{MnCl}_2$ , 2mg ( $10^{-2}$  mmol)  $\text{CrCl}_3$ , 1.00 mL (0.936 g, 8.87 mmol) of deinhibited methyl acrylate, 60 mg (0.175 mmol) 4,4'-di-(5-nonyl)-2,2'-bipyridine [4,4'-di(5-nonyl)-2,2'-bipyridine], and 19 mg ( $8.8 \times 10^{-2}$  mmol) toluenesulphonyl chloride. Two "freeze-pump-thaw" cycles were performed on the contents of the tube to insure that oxygen was removed from the polymerization solution. The tube was sealed under vacuum then placed in an oil bath thermostated at 90 °C. After 7 h the tube was broken, and the content were dissolved in 10 mL of THF. Conversion of the monomer, measured using GC was 98 %, and the molecular weight and polydispersity measured by GPC were  $M_n = 9,900$ , and  $M_w/M_n = 1.59$ .

## **MnCl<sub>2</sub> / CuCl<sub>2</sub> Co-Catalysts**

### **Example 20**

**Homogeneous ATRP of styrene using MnCl<sub>2</sub>/CuCl<sub>2</sub> as catalyst:** The following amounts of reagents were weighed into a glass tube under ambient temperature: 12mg ( $8.15 \times 10^{-2}$  mmol) of MnCl<sub>2</sub>, 2mg ( $10^{-2}$  mmol) CuCl<sub>2</sub>, 1.00 mL (0.909 g, 8.73 mmol) of deinhibited styrene, 60 mg (0.175 mmol) 4,4'-di-(5-nonyl)-2,2'-bipyridine, and 10 mL ( $8.8 \times 10^{-2}$  mmol) 1-phenylethyl chloride. Two "freeze-pump-thaw" cycles were performed on the content of tube to insure that oxygen was removed from the polymerization solution. The tube was sealed under vacuum then placed in an oil bath thermostated at 90 °C. After 12 h the tube was broken, and the contents were dissolved in 10 mL of THF. Conversion of the monomer, measured using GC was 52 %, and the molecular weight and polydispersity measured by GPC were M<sub>n</sub> = 5,300, and M<sub>w</sub>/M<sub>n</sub> = 1.28.

### **Example 21**

**Homogeneous ATRP of methyl acrylate using MnCl<sub>2</sub>/CuCl<sub>2</sub> as catalyst:** The following amounts of reagents were weighed into glass tube under ambient temperature: 12 mg ( $8.15 \times 10^{-2}$  mmol) of MnCl<sub>2</sub>, 2mg ( $10^{-2}$  mmol) CuCl<sub>2</sub>, 1.00 mL (0.956 g, 8.88 mmol) of deinhibited methyl acrylate, 60 mg (0.175 mmol) 4,4'-di-(5-nonyl)-2,2'-bipyridine, and 11 mL ( $8.8 \times 10^{-2}$  mmol) methyl 2-chloropropionate. Two "freeze-pump-thaw" cycles were performed on the contents of the tube to insure that oxygen was removed from the polymerization solution. The tube was sealed under vacuum then placed in an oil bath thermostated at 90 °C. After 12 h the tube was broken, and the content were dissolved in 10 mL of THF. Conversion of the monomer, measured

using GC was 77 %, and the molecular weight and polydispersity measured by GPC were  $M_n = 7,200$ , and  $M_w/M_n = 1.72$ .

### Example 22

**Homogeneous ATRP of methyl methacrylate using  $MnCl_2/CuCl_2$  as catalyst:** The following amounts of reagents were weighed into a glass tube under ambient temperature: 12 mg ( $8.15 \times 10^{-2}$  mmol) of  $MnCl_2$ , 2 mg ( $10^{-2}$  mmol)  $CuCl_2$ , 1.00 mL (0.936 g, 8.87 mmol) of deinhibited methyl acrylate, 60 mg (0.175 mmol) 4,4'-di-(5-nonyl)-2,2'-bipyridine, and 19 mg ( $8.8 \times 10^{-2}$  mmol) toluenesulfonyl chloride. Two "freeze-pump-thaw" cycles were performed on the contents of the tube to insure that oxygen was removed from the polymerization solution. The tube was sealed under vacuum then placed in an oil bath thermostated at 90 °C. After 12 h the tube was broken, and the contents were dissolved in 10 mL of THF. Conversion of the monomer, measured using GC was 78 %, and the molecular weight and polydispersity measured by GPC were  $M_n = 8,200$ , and  $M_w/M_n = 1.37$ .

### New Ligands

#### **Copper (I)**

##### **N,N,N',N",N"-Pentamethyldiethylenetriamine**

### Example 23

**Bulk Polymerization of Styrene with  $CuBr$  /**N,N,N',N",N"-Pentamethyldiethylenetriamine** (PMDETA)/1-Phenylethyl bromide:** The following amounts of reagents were weighed into a glass tube under ambient temperature: 13 mg ( $9.06 \times 10^{-2}$  mmol) of  $CuBr$ , 9.5  $\mu$ l ( $9.06 \times 10^{-2}$  mmol) PMDETA, 12.4  $\mu$ l ( $9.06 \times 10^{-2}$  mmol) (1-bromoethyl)benzene and 1.00 mL (8.73 mmol)

of styrene. Three "freeze-pump-thaw" cycles were performed on the contents of the tube to insure that oxygen was removed from the polymerization solution. The tube was sealed under vacuum and placed in an oil bath thermostated at 90 °C. At the timed interval, polymerization was stopped by cooling the tubes into ice. Afterward, the tube was opened and the contents dissolved in THF.

<b>Sample</b>	<b>Time (h)</b>	<b>Conversion (%)</b>	<b>M<sub>n</sub>, Cal</b>	<b>M<sub>n</sub>, SEC</b>	<b>M<sub>w</sub>/M<sub>n</sub></b>
1	0.75	32	3200	3060	1.47
2	1.40	40	4000	4090	1.40
3	2.53	48	4750	4220	1.33
4	3.50	56	5600	5300	1.27
6	5.30	78	7800	7340	1.35

#### **Example 24**

**Bulk Polymerization of Methyl Acrylate with CuBr /N,N,N',N',N"-Pentamethyldiethylenetriamine (PMDETA)/Ethyl 2-Bromopropionate:** The following amounts of reagents were weighed into a glass tube under ambient temperature: 6.8 mg ( $4.78 \times 10^{-2}$  mmol) of CuBr, 10  $\mu$ l ( $4.78 \times 10^{-2}$  mmol) PMDETA, 6.2  $\mu$ l ( $4.78 \times 10^{-2}$  mmol) ethyl 2-bromopropionate and 1.00 mL (11.1 mmol) of methyl acrylate. Three "freeze-pump-thaw" cycles were performed on the contents of the tube to insure that oxygen was removed from the polymerization solution. The tube was sealed under vacuum and placed in an oil bath thermostated at 90 °C. At the timed interval, polymerization was stopped by cooling the tubes into ice. Afterward, the tube was opened and the contents dissolved in THF.

<b>Sample</b>	<b>Time (h)</b>	<b>Conversion (%)</b>	<b>M<sub>n</sub>, Cal</b>	<b>M<sub>n</sub>, SEC</b>	<b>M<sub>w</sub>/M<sub>n</sub></b>
1	2.0	61	12300	11700	1.13
2	3.0	76	15200	14000	1.13
3	4.7	91	18200	18100	1.20

### **Example 25**

**Solution Polymerization of Methyl Methacrylate with CuBr /N,N,N',N',N"-Pentamethyldiethylenetriamine (PMDETA)/Diethyl 2-Bromo-2-Methylmalonate:** The following amounts of reagents were weighed into a glass tube under ambient temperature: 3.3 mg ( $2.3 \times 10^{-2}$  mmol) of CuBr, 4.9  $\mu$ l ( $2.3 \times 10^{-2}$  mmol) PMDETA, 8.9  $\mu$ l ( $4.7 \times 10^{-2}$  mmol) diethyl 2-bromo-2-methylmalonate, 1.00 mL (9.35 mmol) of methyl acrylate and 1.00 ml of anisole. Three "freeze-pump-thaw" cycles were performed on the contents of the tube to insure that oxygen was removed from the polymerization solution. The tube was sealed under vacuum and placed in an oil bath thermostated at 90 °C. After 0.5 h the tube was broken, and the contents were dissolved in 5 mL of THF. Conversion of the monomer was measured using GC, and the molecular weight and polydispersity were measured by GPC. Conversion was 30%,  $M_n = 8230$  and  $M_w/M_n = 1.23$ .

#### **1.1.4.7.10.10-Hexamethyltriethylenetetramine**

### **Example 26**

**Bulk Polymerization of Styrene with CuBr / 1,1,4,7,10,10-Hexamethyltriethylenetetramine (HMTETA) / 1-Phenylethyl bromide:** The following amounts of reagents were weighed into a glass tube under ambient temperature: 13 mg ( $9.06 \times 10^{-2}$  mmol) of CuBr, 24.8  $\mu$ l ( $9.06 \times 10^{-2}$  mmol) HMTETA, 12.4  $\mu$ l ( $9.06 \times 10^{-2}$  mmol) (1-bromoethyl)benzene and 1.00 mL (8.73 mmol) of styrene. Three "freeze-pump-thaw" cycles were performed on the contents of the tube to insure that oxygen was removed from the polymerization solution. The tube was sealed under vacuum and placed in an oil bath thermostated at 90 °C. After 2.0 h the tube was broken, and the contents were dissolved in 10 mL of THF. Conversion of the monomer was measured using GC, and the molecular weight and polydispersity were measured by GPC. Conversion was 65%,  $M_n = 5590$  and  $M_w/M_n = 1.23$ .

### **Example 27**

**Bulk Polymerization of Methyl Acrylate with CuBr / 1,1,4,7,10,10-Hexamethyltriethylenetetramine (HMTETA)/Ethyl 2-Bromopropionate:** The following amounts of reagents were weighed into a glass tube under ambient temperature: 6.8 mg ( $4.78 \times 10^{-2}$  mmol) of CuBr, 13  $\mu$ l ( $4.78 \times 10^{-2}$  mmol) HMTETA, 6.2  $\mu$ l ( $4.78 \times 10^{-2}$  mmol) ethyl 2-bromopropionate and 1.00 mL (11.1 mmol) of methyl acrylate. Three "freeze-pump-thaw" cycles were performed on the contents of the tube to insure that oxygen was removed from the polymerization solution. The tube was sealed under vacuum and placed in an oil bath thermostated at 90 °C. After 1.6 h the tube was broken, and the contents were dissolved in 5 mL

of THF. Conversion of the monomer was measured using GC, and the molecular weight and polydispersity were measured by GPC. Conversion was 49%,  $M_n = 9150$  and  $M_w/M_n = 1.24$ .

### **Example 28**

**Solution Polymerization of Methyl Methacrylate with CuBr /1,1,4,7,10,10-Hexamethyltriethylenetetramine (HMTETA) / Ethyl 2-Bromoisobutyrate:** The following amounts of reagents were weighed into a glass tube under ambient temperature: 3.3 mg ( $2.3 \times 10^{-2}$  mmol) of CuBr, 6.4  $\mu$ l ( $2.3 \times 10^{-2}$  mmol) HMTETA, 6.1  $\mu$ l ( $4.7 \times 10^{-2}$  mmol) ethyl 2-bromoisobutyrate, 1.00 mL (9.35 mmol) of methyl acrylate and 1.00 ml of anisole. Three "freeze-pump-thaw" cycles were performed on the contents of the tube to insure that oxygen was removed from the polymerization solution. The tube was sealed under vacuum and placed in an oil bath thermostated at 90 °C. After 1.6 h the tube was broken, and the contents were dissolved in 5 mL of THF. Conversion of the monomer was measured using GC, and the molecular weight and polydispersity were measured by GPC. Conversion was 55%,  $M_n = 12900$  and  $M_w/M_n = 1.38$ .

### 1,4,8,11-Tetramethyl-1,4,8,11-Tetraazacyclotetradecane

### **Example 29**

**Bulk Polymerization of Styrene with CuBr / 1,4,8,11-Tetramethyl-1,4,8,11-Tetraazacyclotetradecane (TMTACTD) / 1-Phenylethyl Bromide:** The following amounts of reagents were weighed into a glass tube under ambient temperature: 13 mg ( $9.06 \times 10^{-2}$  mmol)

of CuBr, 23.3 mg ( $9.06 \times 10^{-2}$  mmol) TMTACTD, 12.4  $\mu$ l ( $9.06 \times 10^{-2}$  mmol) (1-bromoethyl)benzene and 1.00 mL (8.73 mmol) of styrene. Three "freeze-pump-thaw" cycles were performed on the contents of the tube to insure that oxygen was removed from the polymerization solution. The tube was sealed under vacuum and placed in an oil bath thermostated at 110 °C. After 2.0 h the tube was broken, and the contents were dissolved in 10 mL of THF. Conversion of the monomer was measured using GC, and the molecular weight and polydispersity were measured by GPC. Conversion was 47%,  $M_n = 4780$  and  $M_w/M_n = 1.72$ .

### 8 - Hydroxyquinoline

#### **Example 30**

**ATRP of Styrene Using CuBr / Bipy / 8 - Hydroxyquinoline:** The following amounts of reagents were weighed into a glass tube under ambient temperature: 12 mg ( $8.15 \times 10^{-2}$  mmol) of CuBr, 1.00 mL (0.909 g, 8.73 mmol) of deinhibited styrene, 14 mg (0.08 mmol) 2,2'-bipyridine, 12 mg (0.08 mmol) 8-hydroxyquinoline, and 12 mL ( $8.8 \times 10^{-2}$  mmol) 1 - phenylethyl bromide. Two "freeze-pump-thaw" cycles were performed on the contents of the tube to ensure that oxygen was removed from the polymerization solution. The tube was sealed under vacuum and then placed in an oil bath thermostated at 90 °C. After 7 h the tube was broken, and the contents were dissolved in 10 mL of THF. Conversion of the monomer, as measured using GC, was 28 %, and the molecular weight and polydispersity (GPC) were  $M_n = 3,200$ , and  $M_w/M_n = 1.21$ .

#### **Example 31**

**ATRP of Methyl Acrylate Using CuBr / Bipy / 8 - Hydroxyquinoline:** The following amounts of reagents were weighed into a glass tube under ambient temperature: 12mg ( $8.15 \times 10^{-2}$  mmol) of CuBr, 1.00 mL (0.956 g, 8.88 mmol) of deinhibited methyl acrylate, 14 mg (0.08 mmol) 2,2'-

bipyridine, 12 mg (0.08 mmol) 8-hydroxy quinoline, and 12 mL ( $8.8 \times 10^{-2}$  mmol) methyl 2-bromopropionate. Two “freeze-pump-thaw” cycles were performed on the contents of the tube to ensure that oxygen was removed from the polymerization solution. The tube was sealed under vacuum and placed in an oil bath thermostated at 90 °C. After 4 h the tube was broken, and the contents were dissolved in 10 mL of THF. Conversion of the monomer, as determined by GC was 50 %, and the molecular weight and polydispersity, measured by GPC, were  $M_n = 5,200$  and  $M_w/M_n = 1.25$ .

### **Example 32**

**ATRP of Methyl Methacrylate Using CuBr / Bipy / 8 - Hydroxyquinoline:** The following amounts of reagents were weighed into glass tube under ambient temperature: 12mg ( $8.15 \times 10^{-2}$  mmol) of CuBr, 1.00 mL (0.936 g, 8.87 mmol) of deinhibited methyl acrylate, 14 mg (0.08 mmol) 2,2'-bipyridine, 12 mg (0.08 mmol) 8-hydroxy quinoline, and 19 mg ( $8.8 \times 10^{-2}$  mmol) p-toluenesulfonyl chloride. Two “freeze-pump-thaw” cycles were performed on the contents of the tube to ensure that oxygen was removed from the polymerization solution. The tube was sealed under vacuum and placed in an oil bath thermostated at 90 °C. After 4 h the tube was broken, and the contents were dissolved in 10 mL of THF. Conversion of the monomer, as determined by GC was 75 %, and the molecular weight and polydispersity, measured by GPC, were  $M_n = 7,800$ , and  $M_w/M_n = 1.29$ .

### Tetramethylethylenediamine

### **Example 33**

**Bulk Polymerization by ATRP using CuBr / tetramethylethylenediamine:** To a dry schlenk flask under argon, CuBr (127.1 mg, 0.874 mmol), tetramethylethylenediamine (264  $\mu$ L, 1.75

mmol), degassed styrene (10.0 ml, 87.4 mmol) and 1 - phenylethyl bromide (119.3 uL, 0.874 mmol) were added. The solution was allowed to stir at room temperature until it became homogeneous and then transferred to dry glass tubes under argon. Three freeze-pump-thaw cycles were performed, the tubes were sealed under vacuum, and then placed in an oil bath thermostated at the desired temperature. Tubes were removed at timed intervals and the polymerization quenched by cooling the tubes in ice. Afterward, the tubes were opened and the contents dissolved in THF.

<b>Sample</b>	<b>Time (h)</b>	<b>Conversion (%)</b>	<b>M<sub>n</sub>, Cal</b>	<b>M<sub>n</sub>, SEC</b>	<b>M<sub>w</sub>/M<sub>n</sub></b>
1	1.0	6.1	610	1,100	1.95
2	2.0	24.5	2,500	2,800	1.62
3	3.1	35.9	3,600	4,000	1.53
4	5.1	54.4	5,400	6,800	1.50
5	6.8	76.7	7,700	9,100	1.57

#### **Example 34**

**Bulk Polymerization by ATRP using CuBr / tetramethylethylenediamine:** To a dry schlenk flask under argon, CuBr (71.3 mg, 0.49 mmol), tetramethylethylenediamine (148 uL, 0.98 mmol), degassed methyl acrylate (10.0 ml, 111.2 mmol) and ethyl 2-bromopropionate (63.6 uL, 0.49 mmol) were added. The solution was allowed to stir at room temperature until it became homogeneous and then transferred to dry glass tubes under argon. Three freeze-pump-thaw cycles were performed, the tubes were sealed under vacuum, and then placed in an oil bath thermostated at the desired temperature. Tubes were removed at timed intervals and the polymerization quenched by cooling the tubes in ice. Afterward, the tubes were opened and the contents dissolved in THF.

<b>Sample</b>	<b>Time (h)</b>	<b>Conversion (%)</b>	<b>M<sub>n</sub>, Cal</b>	<b>M<sub>n</sub>, SEC</b>	<b>M<sub>w</sub>/M<sub>n</sub></b>

1	1.0	21.3	4,300	4,600	1.55
2	2.0	55.5	11,100	11,200	1.31
3	2.6	74.6	14,900	14,100	1.37
4	3.3	83.2	16,600	15,400	1.39
5	4.6	91.9	18,400	17,100	1.51

### Example 35

34.0 mg (0.234 mmol) CuBr, 5.0 ml(46.8 mmol) methyl methacrylate, 70.6  $\mu$ l (0.468 mmol) tetramethylethylenediamine, and 5.0 ml anisole were added to a dry round-bottomed flask under an argon atmosphere. After the mixture was stirred until homogeneous, 34.3  $\mu$ l (0.234 mmol) ethyl 2-bromo isobutyrate was added to the flask which was then immersed in an oil bath thermostated at the desired temperature. A positive argon pressure was maintained throughout the reaction and samples were withdrawn at timed intervals.

Sample	Time (h)	Conversion (%)	Mn, Cal	Mn, SEC	Mw/Mn
1	0.4	7.4	1,500	4,300	1.33
2	1.0	28.2	5,600	8000	1.27
3	1.6	49.0	9,800	10,700	1.26
4	2.2	61.9	12,400	13,100	1.30
5	3.0	76.7	15,300	15,600	1.29
6	3.4	80.4	16,100	15,900	1.37
7	4.1	85.9	17,200	18,300	1.35
8	5.0	88.9	17,800	17,300	1.42
9	5.8	91.1	18,200	17,800	1.46

### Iron (II)

#### NR<sub>3</sub> Ligands

### Example 36

**Bulk Polymerization using FeBr<sub>2</sub> / 4,4'-di(5-nonyl)-2,2'-bipyridine / NBu<sub>3</sub>:** The following reagents were transferred into glass tubes purged with argon: 19.0 mg (8.73 x 10<sup>-2</sup> mmol) of

$\text{FeBr}_2$ , 1.0 ml (8.73 mmol) of styrene, 12.0 ml ( $8.73 \times 10^{-2}$  mmol) of 1-phenylethyl bromide, 35.6 mg ( $8.73 \times 10^{-2}$  mmol) of 4,4'-di(5-nonyl)-2,2'-bipyridine and 21.0 ml ( $8.73 \times 10^{-2}$  mmol) of tri(n-butyl)amine. Each tube was degassed three times by "freeze-pump-thaw" cycles and sealed under vacuum. The tubes were placed in an oil bath thermostated at 110 °C and were removed from the oil bath at timed intervals.

Sample	Time(hr)	Conv. (%)	$M_n$ (th.)	$M_n$ (GPC)	$M_w / M_n$
1	1.5	30.7	3,200	3,200	1.15
2	3.0	48.5	5,000	5,100	1.11
3	5.0	67.2	7,000	7,200	1.13
4	8.0	87.1	9,100	9,800	1.20

### Example 37

**Solution Polymerization of  $\text{FeBr}_2$  /  $\text{NBu}_3$ :** The following reagents were transferred into a 25 ml schlenk flask equipped with a magnetic stir bar under an argon atmosphere: 95.0 mg (0.436 mmol) of  $\text{FeBr}_2$ , 5.0 ml (43.6 mmol) of styrene, 60.0 ml (0.436 mmol) of 1-phenylethyl bromide, 310 ml (1.3 mmol) of tri(n-butyl)amine and 5.0 ml o-xylene. The solution was stirred at room temperature for 20 minutes and then the flask was put into an oil bath thermostated at 110 °C. A positive argon pressure was maintained throughout the reaction and samples were withdrawn at time intervals. The polymerization solution was heterogeneous.

Sample	Time(hr)	Conv. (%)	$M_n$ (th.)	$M_n$ (GPC)	$M_w / M_n$
1	2.0	26.3	2,700	3,100	1.43
2	5.0	42.8	4,400	4,300	1.19
3	15.0	62.8	6,500	5,900	1.16
4	24.0	69.3	7,200	7,200	1.17

### Example 38

**Bulk Polymerization of Styrene with  $\text{FeBr}_2$  /  $\text{N}(\text{n-Octyl})_3$  / 1 - phenylethylbromide:** A dry round-bottomed flask was charged with  $\text{FeBr}_2$  (95.0 mg, 0.436 mmol). The flask was sealed with a rubber septum and was cycled between vacuum and argon three times to remove the oxygen. Degassed styrene (10.0 ml, 87.3 mmol),  $\text{N}(\text{n-Octyl})_3$  (0.38 ml, 0.87 mmol) and 1-phenylethyl bromide (0.06 ml, 0.436 mmol) were added using degassed syringes and stainless steel needles. The flask was immersed in an oil

bath held by a thermostat at 110 °C. At the timed intervals, a sample was withdrawn from the flask using a degassed syringe and added to THF.

<b>Sample</b>	<b>Time (h)</b>	<b>Conversion (%)</b>	<b>M<sub>n</sub>, Cal</b>	<b>M<sub>n</sub>, SEC</b>	<b>M<sub>w</sub>/M<sub>n</sub></b>
1	1.0	20	4100	4700	1.35
2	2.0	29	6000	6700	1.29
3	3.0	36	7500	8200	1.27
4	4.0	42	8800	9100	1.27
5	5.0	51	10500	11300	1.26
6	6.0	54	11300	12700	1.27
7	9.0	63	13200	15800	1.26

**Example 39**

**Solution Polymerization of Styrene with FeBr<sub>2</sub> /N(n-Octyl)<sub>3</sub> / Tetrabutylammonium bromide / 1 - phenylethylbromide:** A dry round-bottomed flask was charged with FeBr<sub>2</sub> (95.0 mg, 0.436 mmol) and N(n-Bu)<sub>4</sub>Br (70.0 mg, 0.22 mmol). The flask was sealed with a rubber septum and was cycled between vacuum and argon three times to remove the oxygen. Degassed styrene (5.0 ml, 43.6 mmol), N(n-Octyl)<sub>3</sub> (0.38 ml, 0.87 mmol), 1-phenylethylbromide (0.06 ml, 0.436 mmol) and o - xylene (5.0 ml) were added using degassed syringes and stainless steel needles. The flask was immersed in an oil bath held by a thermostat at 110 °C. At the timed intervals, a sample was withdrawn from the flask using a degassed syringe and added to THF.

<b>Sample</b>	<b>Time (h)</b>	<b>Conversion (%)</b>	<b>M<sub>n</sub>, Cal</b>	<b>M<sub>n</sub>, SEC</b>	<b>M<sub>w</sub>/M<sub>n</sub></b>
1	1.0	27	2800	2700	1.20
2	2.0	35	3600	3700	1.18
3	4.0	44	4600	4700	1.16
4	6.0	49	5100	5500	1.14
5	8.0	53	5600	6100	1.15
6	11.0	57	6000	7000	1.14

**Example 40**

**Solution Polymerization using  $\text{FeBr}_2$  /  $\text{NBu}_3$  / p-toluenesulfonyl chloride:** 34.0 mg (0.18 mmol) of  $\text{FeBr}_2$ , 5.0 ml (53.5 mmol) of methyl methacrylate, 112 ml (0.53 mmol) of tri(n-butyl)amine and 4.0 ml o-xylene were transferred into a 25ml schlenk flask equipped with a magnetic stir bar under an argon atmosphere. The solution was stirred at room temperature for 20 minutes, and 30 mg (0.18 mmol) of p-toluenesulfonyl chloride in 1.0 ml of o-xylene was added to the flask. The flask was put into an oil bath thermostated at 80 °C. A positive argon pressure was maintained throughout the reaction and samples were withdrawn at time intervals. The polymerization solution was heterogeneous.

<b>Sample</b>	<b>Time(hr)</b>	<b>Conv. (%)</b>	<b><math>M_n</math> (th.)</b>	<b><math>M_n</math> (GPC)</b>	<b><math>M_w / M_n</math></b>
1	0.5	18.0	5,400	5,600	1.71
2	1.0	33.3	10,000	12,400	1.66
3	2.0	49.4	14,800	17,500	1.69
4	3.0	58.3	17,500	19,000	1.69
5	4.0	67.7	20,300	21,300	1.69
6	5.0	77.9	23,400	25,600	1.60

**Example 41**

**Solution Polymerization using  $\text{FeBr}_2$  / 4,4'-di(5-nonyl)-2,2'-bipyridine /  $\text{NBu}_3$  / p-toluenesulfonyl chloride:** 34.0 mg (0.18 mmol) of  $\text{FeBr}_2$ , 5.0 ml (53.5 mmol) of methyl methacrylate, 37 ml (0.18 mmol) of tri(n-butyl)amine, 64.0 mg (0.18 mmol) 4,4'-di(5-nonyl)-2,2'-bipyridine and 4.0 ml o-xylene were transferred into a 25 ml schlenk flask equipped with a magnetic stir bar under an argon atmosphere. The solution was stirred at room temperature for 20 minutes, and 30 mg (0.18 mmol) of p-toluenesulfonyl chloride in 1.0 ml of o-xylene was added to the flask. The flask was put into an oil bath thermostated at 80 °C. A positive argon pressure was maintained throughout the reaction and samples were withdrawn at time intervals. The polymerization solution was homogeneous.

<b>Sample</b>	<b>Time(hr)</b>	<b>Conv. (%)</b>	<b><math>M_n</math> (th.)</b>	<b><math>M_n</math> (GPC)</b>	<b><math>M_w / M_n</math></b>
1	1.0	15.0	7,500	7,400	1.28
2	2.0	31.3	9,400	11,600	1.36

3	4.5	51.2	15,400	17,900	1.38
4	8.0	67.8	20,300	19,900	1.38
5	24.0	88.5	26,600	27,100	1.33

### Example 42

**Solution Polymerization of MMA with  $\text{FeBr}_2$  /  $\text{N}(\text{n-Octyl})_3$  / p - toluenesulfonyl chloride:** A dry round-bottomed flask was charged with  $\text{FeBr}_2$  (34.0 mg, 0.16 mmol). The flask was sealed with a rubber septum and was cycled between vacuum and argon three times to remove the oxygen. Degassed methyl methacrylate (5.0 ml, 46.7 mmol), o - xylene (4.0 ml) and  $\text{N}(\text{n-Octyl})_3$  (0.14 ml, 0.32 mmol) were added using degassed syringes and stainless steel capillaries. The o - toluenesulfonyl chloride (30.0 mg, 0.16 mmol) was added as a solution in o-xylene (1.0 ml) and the flask was immersed in an oil bath held by a thermostat at 80 °C. At the timed intervals, a sample was withdrawn from the flask using a degassed syringe and added to THF.

Sample	Time (h)	Conversion (%)	$M_n$ , Cal	$M_n$ , SEC	$M_w/M_n$
1	1.0	22	6450	7000	1.45
2	2.0	35	10400	15000	1.43
3	3.0	47	14000	18800	1.46
4	4.0	53	16000	21100	1.48
5	5.5	61	18300	23500	1.46
6	7.0	66	19900	25300	1.44
7	10.0	75	22400	27300	1.40

### Example 43

**Solution Polymerization of MMA with  $\text{FeBr}_2$  /  $\text{N}(\text{n-Octyl})_3$  / p - toluenesulfonyl chloride:** A dry round-bottomed flask was charged with  $\text{FeBr}_2$  (34.0 mg, 0.16 mmol) and  $\text{N}(\text{n-Bu})_4\text{Br}$  (17.0 mg, 0.5 mmol). The flask was sealed with a rubber septum and was cycled between vacuum and argon three times to remove the oxygen. Degassed methyl methacrylate (5.0 ml, 46.7 mmol), o - xylene (4.0 ml) and  $\text{N}(\text{n-Octyl})_3$  (0.14 ml, 0.32 mmol) were added using degassed syringes and stainless steel capillaries. The o - toluenesulfonyl chloride (30.0 mg, 0.16 mmol) was added as a solution in o-xylene (1.0 ml) and the flask

was immersed in an oil bath held by a thermostat at 80 °C. At the timed intervals, a sample was withdrawn from the flask using a degassed syringe and added to THF.

<u>Sample</u>	<u>Time (h)</u>	<u>Conversion (%)</u>	<u>M<sub>n</sub>, Cal</u>	<u>M<sub>n</sub>, SEC</u>	<u>M<sub>w</sub>/M<sub>n</sub></u>
1	1.0	17	5000	6900	1.43
2	2.0	28	8400	11900	1.43
3	3.0	37	11100	15400	1.42
4	4.5	47	14200	19100	1.40
5	6.0	59	17500	22500	1.37
6	8.8	70	21100	25600	1.37
7	10.0	74	22300	26100	1.37

#### Example 44

##### **Solution Polymerization of MMA with FeBr<sub>2</sub> / FeBr<sub>3</sub> / N(n-Octyl)<sub>3</sub> / p - toluenesulfonyl chloride:**

A dry round-bottomed flask was charged with FeBr<sub>2</sub> (34.0 mg, 0.16 mmol) and FeBr<sub>3</sub> (4.7 mg, 0.016 mmol). The flask was sealed with a rubber septum and was cycled between vacuum and argon three times to remove the oxygen. Degassed methyl methacrylate (5.0 ml, 46.7 mmol), o - xylene (4.0 ml) and N(n-Octyl)<sub>3</sub> (0.14 ml, 0.32 mmol) were added using degassed syringes and stainless steel capillaries. The o - toluenesulfonyl chloride (30.0 mg, 0.16 mmol) was added as a solution in o-xylene (1.0 ml) and the flask was immersed in an oil bath held by a thermostat at 80 °C. At the timed intervals, a sample was withdrawn from the flask using a degassed syringe and added to THF.

<u>Sample</u>	<u>Time (h)</u>	<u>Conversion (%)</u>	<u>M<sub>n</sub>, Cal</u>	<u>M<sub>n</sub>, SEC</u>	<u>M<sub>w</sub>/M<sub>n</sub></u>
1	1.0	14	4100	4700	1.43
2	2.0	27	8100	9700	1.40
3	3.0	39	11600	13000	1.46
4	4.5	49	14700	16200	1.46
5	6.0	57	17100	18700	1.45
6	12.0	71	21200	23300	1.44
7	29.0	86	25800	26900	1.42

### PR<sub>3</sub> Ligands

#### Example 45

**Bulk Polymerization using FeBr<sub>2</sub> / PBu<sub>3</sub>:** The following reagents were transferred into glass tubes purged with argon: 9.5 mg ( $4.36 \times 10^{-2}$  mmol) of FeBr<sub>2</sub>, 1.0 ml (8.73 mmol) of styrene, 6.0 ml ( $4.36 \times 10^{-2}$  mmol) of 1-phenylethyl bromide and 32.4 ml ( $13.1 \times 10^{-2}$  mmol) of tri(n-butyl)phosphine. Each tube was degassed three times by "freeze-pump-thaw" cycles and sealed under vacuum. The tubes were placed in an oil bath thermostated at 110 °C and were removed from the oil bath at timed intervals.

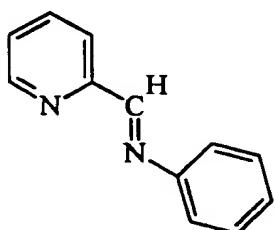
<b>Sample</b>	<b>Time(hr)</b>	<b>Conv. (%)</b>	<b>M<sub>n</sub> (th.)</b>	<b>M<sub>n</sub> (GPC)</b>	<b>M<sub>w</sub> / M<sub>n</sub></b>
1	1.0	25.6	5,300	4,700	1.55
2	2.0	41.5	8,600	9,600	1.30
3	3.0	59.6	12,400	13,200	1.43
4	4.0	69.4	14,400	15,800	1.40

#### Example 46

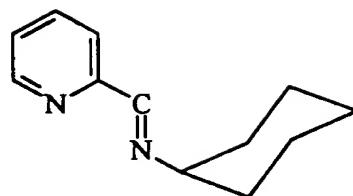
**Bulk Polymerization using FeBr<sub>2</sub> / 4,4'-di(5-nonyl)-2,2'-bipyridine / PBu<sub>3</sub>:** The following reagents were transferred into glass tubes purged with argon: 19.0 mg ( $8.73 \times 10^{-2}$  mmol) of FeBr<sub>2</sub>, 1.0 ml (8.73 mmol) of styrene, 12.0 ml ( $8.73 \times 10^{-2}$  mmol) of 1-phenylethyl bromide, 35.6 mg ( $8.73 \times 10^{-2}$  mmol) of 4,4'-di(5-nonyl)-2,2'-bipyridine and 21.6 ml ( $8.73 \times 10^{-2}$  mmol) of tri(n-butyl)phosphine. Each tube was degassed three times by "freeze-pump-thaw" cycles and sealed under vacuum. The tubes were placed in an oil bath thermostated at 110 °C and were removed from the oil bath at timed intervals.

<b>Sample</b>	<b>Time(hr)</b>	<b>Conv. (%)</b>	<b>M<sub>n</sub> (th.)</b>	<b>M<sub>n</sub> (GPC)</b>	<b>M<sub>w</sub> / M<sub>n</sub></b>
1	1.0	28.9	3,000	2,100	1.34
2	2.0	39.3	4,100	4,600	1.15
3	3.0	59.8	6,200	6,400	1.12
4	4.0	68.4	7,100	7,900	1.12
5	5.0	82.1	8,500	9,600	1.13

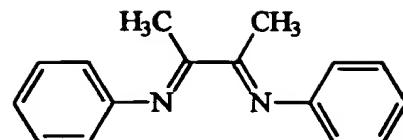
## Miscellaneous Ligands



L-1



L-2



L-3

### Example 47

The following reagents were transferred into a glass tube purged with argon: 19.0 mg ( $8.73 \times 10^{-2}$  mmol) of  $\text{FeBr}_2$ , 1.0 ml (8.73 mmol) of styrene, 12.0 ml ( $8.73 \times 10^{-2}$  mmol) of 1-phenylethyl bromide and ligand L1 ( $17.5 \times 10^{-2}$  mmol). Each tube was degassed three times by "freeze-pump-thaw" cycles and sealed under vacuum. The tube was placed in an oil bath thermostated at 110 °C and was removed from the oil bath after 5.0 h. The conversion was 42 % as determined by gas chromatography.  $M_n, \text{theory} = 4,400$ ;  $M_n, \text{GPC} = 7,700$ ;  $M_w / M_n = 1.3$ .

### Example 48

The following reagents were transferred into a glass tube purged with argon: 19.0 mg ( $8.73 \times 10^{-2}$  mmol) of  $\text{FeBr}_2$ , 1.0 ml (8.73 mmol) of styrene, 12.0 ml ( $8.73 \times 10^{-2}$  mmol) of 1-phenylethyl bromide and ligand L2 ( $17.5 \times 10^{-2}$  mmol). Each tube was degassed three times by "freeze-pump-thaw" cycles and sealed under vacuum. The tube was placed in an oil bath thermostated at 110 °C and was removed from the oil bath after 24.0 h. The conversion was 47 % as determined by gas chromatography.  $M_n, \text{theory} = 4,900$ ;  $M_n, \text{GPC} = 6,300$ ;  $M_w / M_n = 1.3$ .

### Example 49

The following reagents were transferred into a glass tube purged with argon: 19.0 mg ( $8.73 \times 10^{-2}$  mmol) of  $\text{FeBr}_2$ , 1.0 ml (8.73 mmol) of styrene, 12.0 ml ( $8.73 \times 10^{-2}$  mmol) of 1-phenylethyl

bromide and ligand **L3** ( $17.5 \times 10^{-2}$  mmol). Each tube was degassed three times by "freeze-pump-thaw" cycles and sealed under vacuum. The tube was placed in an oil bath thermostated at 110 °C and was removed from the oil bath after 2.5 h. The conversion was 90 % as determined by gas chromatography.  $M_{n, \text{theory}} = 9,300$ ;  $M_{n, \text{GPC}} = 11,600$ ;  $M_w / M_n = 2.1$ .

### **Example 50**

The following reagents were transferred into a glass tube purged with argon: 19.0 mg ( $8.73 \times 10^{-2}$  mmol) of  $\text{FeBr}_2$ , 1.0 ml (8.73 mmol) of styrene, 12.0 ml ( $8.73 \times 10^{-2}$  mmol) of 1-phenylethyl bromide and 26.4  $\mu\text{L}$  tetramethylethylenediamine, ( $17.5 \times 10^{-2}$  mmol). Each tube was degassed three times by "freeze-pump-thaw" cycles and sealed under vacuum. The tube was placed in an oil bath thermostated at 110 °C and was removed from the oil bath after 6.0 h. The conversion was 61 % as determined by gas chromatography.  $M_{n, \text{theory}} = 6,300$ ;  $M_{n, \text{GPC}} = 7,500$ ;  $M_w / M_n = 1.6$ .

### **Effect of Ligand**

### **ABC\* Polymerizations**

#### **Example 51**

**Use of 4,4'-di(5-nonyl)-2,2'-bipyridine / CuBr:** To a 10 ml round bottom flask with a stir bar, 4, 4' - di(5 - nonyl) - 2, 2' - bipyridine (244.8 mg, 0.6 mmol) and CuBr (43.6 mg, 0.3 mmol) were added and sealed with a rubber septum. The contents of the flask were degassed by applying a vacuum and backfilling with nitrogen (3X). Degassed 2 - (2 - bromopropionyloxy)ethyl acrylate (5.0 ml, 30.9 mmol) was added via syringe. The reaction mixture was stirred in a 100 °C oil bath. After 4 days, no polymer was obtained and the reaction mixture had turned from dark red to dark green.

#### **Example 52**

**Use of Bipy / CuBr, 100 °C:** To a 10 ml round bottom flask with a stir bar, bipyridine (173.9 mg, 1.11 mmol), CuBr (53.8 mg, 0.37 mmol) and dimethoxybenzene (600 mg) were added and sealed with a rubber septum. The contents of the flask were degassed by applying a vacuum and

backfilling with nitrogen (3X). Degassed 2 - (2 - bromopropionyloxy)ethyl acrylate (6.0 ml, 37.1 mmol) was added via syringe. The reaction mixture was stirred in a 100 °C oil bath. Samples were taken at various intervals to monitor conversion and molecular weight. C is a measure of the degree of branching; for a perfect system, C = 0.63 at conversion = 1.0.

Time (h)	Conversion(GC, %)	$M_n$ , SEC	$M_w / M_n$	$C / (C+C^*)$
0.5	>99	5,400	1.98	
1.0	>99	5,300	1.99	
2.5	>99	7,900	1.55	.361

### Example 53

**Use of Bipy / CuBr, 80 °C:** To a 10 ml round bottom flask with a stir bar, bipyridine (173.9 mg, 1.11 mmol), CuBr (53.8 mg, 0.37 mmol) and dimethoxybenzene (600 mg) were added and sealed with a rubber septum. The contents of the flask were degassed by applying a vacuum and backfilling with nitrogen (3X). Degassed 2 - (2 - bromopropionyloxy)ethyl acrylate (6.0 ml, 37.1 mmol) was added via syringe. The reaction mixture was stirred in a 80 °C oil bath. Samples were taken at various intervals to monitor conversion and molecular weight. C is a measure of the degree of branching; for a perfect system, C = 0.63 at conversion = 1.0.

Time (h)	Conversion(GC, %)	$M_n$ , SEC	$M_w / M_n$	$C / (C+C^*)$
0.5	98	7,800	1.75	0.238
1.0	>99	9,000	1.68	0.277
2.5	>99	8,200	1.76	0.268

### Example 54

**Use of Bipy / CuBr, 50 °C:** To a 10 ml round bottom flask with a stir bar, bipyridine (173.9 mg, 1.11 mmol), CuBr (53.8 mg, 0.37 mmol) and dimethoxybenzene (600 mg) were added and sealed with a rubber septum. The contents of the flask were degassed by applying a vacuum and backfilling with nitrogen (3X). Degassed 2 - (2 - bromopropionyloxy)ethyl acrylate (6.0 ml, 37.1

mmol) was added via syringe. The reaction mixture was stirred in a 50 °C oil bath. Samples were taken at various intervals to monitor conversion and molecular weight. C is a measure of the degree of branching; for a perfect system, C = 0.63 at conversion = 1.0.

Time (h)	Conversion(GC, %)	M <sub>n</sub> , SEC	M <sub>w</sub> / M <sub>n</sub>	C / (C+C*)
0.5	5.7	2,400	5.48	
1.0	31.0	13,700	10.2	
1.5	45.5	23,200	2.57	0.277
2.0	55.1	27,700	2.87	

### Example 55

**Use of dTBipy / CuBr, 50 °C:** To a 10 ml round bottom flask with a stir bar, 4, 4' - di(t-butyl) - 4, 4'- bipyridine (223.5 mg, 0.834 mmol), CuBr (40.4 mg, 0.278 mmol) and dimethoxybenzene (500 mg) were added and sealed with a rubber septum. The contents of the flask were degassed by applying a vacuum and backfilling with nitrogen (3X). Degassed 2 - (2 - bromopropionyloxy)ethyl acrylate (4.5 ml, 27.8 mmol) was added via syringe. The reaction mixture was stirred in a 50 °C oil bath. Samples were taken at various intervals to monitor conversion and molecular weight. C is a measure of the degree of branching; for a perfect system, C = 0.63 at conversion = 1.0.

Time (h)	Conversion(GC, %)	M <sub>n</sub> , SEC	M <sub>w</sub> / M <sub>n</sub>	C / (C+C*)
0.5	1.0	200	1.37	0.142
1.0	2.5	220	1.49	0.143
1.5	4.7	250	1.89	0.192
2.0	18.2	380	4.85	0.272
3.0	56.3	820	6.55	0.501
4.0	85.3	1560	6.31	0.387
5.0	95.2	2050	6.33	0.420
6.0	>99	2050	6.89	0.430

## Counter Ions (Cu-X)

### Comparision Polymerizations

#### Example 56

**Polymerization of Methyl Acrylate by ATRP Using CuBr:** Stock solutions were prepared with methyl acrylate (8.0 ml), CuBr (1.3 mg), 4, 4' - di(5 - nonyl) - 2, 2' - bipyridine (7.3 mg), and methyl 2 - bromopropionate (21.2 uL). These stock solutions were transferred to glass tubes and degassed by freeze - pump - thaw. The tubes were then sealed under vacuum and heated in a 90 °C oil bath. The tubes were removed at various intervals and analyzed for conversion (GC) and molecular weight (SEC).

Time (hr)	Conversion (%)	$\ln [M]_0/[M]$	$M_n$	$M_w/M_n$	$M_n$ theo
1.07	18.4	0.20	8,200	1.39	
3.07	43.2	0.57	14,200	1.17	
5.60	84.2	1.84	26,200	1.14	
8.65	96.3	3.30	28,000	1.20	38,500

$\text{PF}_6^-$

### Styrene

#### Example 57

**Initiated with Benzyl Thiocyanate:** Stock solutions were prepared and subsequently distributed to glass tubes which were degassed three times by the freeze-thaw method and sealed under vacuum. Stock solutions consisted of previously degassed monomer,  $\text{CuPF}_6^-$ , 4,4'-di(5-nonyl)-2,2'-bipyridine, and initiator. The solution containing styrene (8 ml, 88.9 mmol),  $\text{CuPF}_6^-$  (0.26 g, 0.7 mmol), and 4,4'-di(5-nonyl)-2,2'-bipyridine (0.5704g, 1.4 mmol) was stirred until homogeneous after which benzyl thiocyanate (0.175 mmol) was added and the solution transferred to the tubes. The tubes were places in an oil bath thermostated at 100 °C.

Time (hr)	Conversion (%)	$\ln [M]_0/[M]$	$M_n$	$M_w/M_n$	$M_n$ theo
0.45	22.1	0.25	54,600	2.16	
1.60	26.2	0.30	60,800	1.91	
3.80	43.7	0.57	46,400	2.13	
5.95	51.7	0.73	40,100	2.41	
7.90	69.3	1.18	48,000	2.34	
10.00	89.5	2.26	53,000	2.57	35,800

### Example 58

**Initiated with 1 - Phenylethyl chloride:** Stock solutions were prepared and subsequently distributed to glass tubes which were degassed three times by the freeze-thaw method and sealed under vacuum. Stock solutions consisted of previously degassed monomer, CuPF<sub>6</sub>, 4,4'-di(5-nonyl)-2,2'-bipyridine, and initiator. The solution containing styrene (8 ml, 88.9 mmol), CuPF<sub>6</sub> (0.26 g, 0.7 mmol), and 4,4'-di(5-nonyl)-2,2'-bipyridine (0.5704g, 1.4 mmol) was stirred until homogeneous after which 1 - phenylethyl chloride (0.175 mmol) was added and the solution transferred to the tubes. The tubes were places in an oil bath thermostated at 100 °C.

Time (hr)	Conversion (%)	$\ln [M]_0/[M]$	$M_n$	$M_w/M_n$	$M_n$ theo
0.45	26.5	0.31	5,700	1.62	
1.48	30.6	0.37	10,300	1.36	
3.55	60.3	0.92	22,000	1.24	
5.40	77.4	1.49	28,500	1.29	
7.50	79.3	1.58	33,700	1.23	
9.77	97.0	3.50	37,800	1.36	38,800

### Example 59

**Initiated with 1 - Phenylethyl bromide:** Stock solutions were prepared and subsequently distributed to glass tubes which were degassed three times by the freeze-thaw method and sealed under vacuum. Stock solutions consisted of previously degassed monomer, CuPF<sub>6</sub>, 4,4'-di(5-nonyl)-2,2'-bipyridine, and initiator. The solution containing styrene (8 ml, 88.9 mmol), CuPF<sub>6</sub>

(0.26 g, 0.7 mmol), and 4,4'-di(5-nonyl)-2,2'-bipyridine (0.5704g, 1.4 mmol) was stirred until homogeneous after which 1 - phenylethyl bromide (0.175 mmol) was added and the solution transferred to the tubes. The tubes were places in an oil bath thermostated at 100 °C.

Time (hr)	Conversion (%)	$\ln [M]_0/[M]$	$M_n$	$M_w/M_n$	$M_n$ theo
0.52	28.6	0.34	15,800	1.31	
1.53	44.2	0.58	29,000	1.66	
2.47	51.1	0.72	37,100	1.87	
3.50	70.1	1.21	46,500	2.51	
4.57	63.4	1.01	41,800	2.13	
5.68	83.5	1.80	52,100	2.83	33,400

### Example 60

**Initiated with Methyl 2 - Iodopropionate:** Stock solutions were prepared and subsequently distributed to glass tubes which were degassed three times by the freeze-thaw method and sealed under vacuum. Stock solutions consisted of previously degassed monomer, CuPF<sub>6</sub>, 4,4'-di(5-nonyl)-2,2'-bipyridine, and initiator. The solution containing styrene (8 ml, 88.9 mmol), CuPF<sub>6</sub> (0.26 g, 0.7 mmol), and 4,4'-di(5-nonyl)-2,2'-bipyridine (0.5704g, 1.4 mmol) was stirred until homogeneous after which methyl 2 - iodopropionate (0.175 mmol) was added and the solution transferred to the tubes. The tubes were places in an oil bath thermostated at 100 °C.

Time (hr)	Conversion (%)	$\ln [M]_0/[M]$	$M_n$	$M_w/M_n$	$M_n$ theo
0.58	27.2	0.32	19,600	2.79	
1.55	36.8	0.46	22,900	3.69	
3.60	52.0	0.73	38,800	3.33	
5.63	58.2	0.87	46,100	3.31	
7.58	58.7	0.88	38,200	3.91	23,500

### Methyl Acrylate

#### **Example 61**

**Initiated with benzyl thiocyanate:** Stock solutions were prepared with methyl acrylate (8.0 ml), CuPF<sub>6</sub> (330.7 mg), 4, 4' - di(5 - nonyl) - 2, 2' - bipyridine (725.4 mg), and benzyl thiocyanate (28.5 mg). These stock solutions were transferred to glass tubes and degassed by freeze - pump - thaw. The tubes were then sealed under vacuum and heated in a 90 °C oil bath. The tubes were removed at various intervals and analyzed for conversion (GC) and molecular weight (SEC).

<b>Time (hr)</b>	<b>Conversion (%)</b>	<b>ln [M]<sub>0</sub>/[M]</b>	<b>M<sub>n</sub></b>	<b>M<sub>w</sub> / M<sub>n</sub></b>	<b>M<sub>n</sub> theo</b>
0.52	27.3	0.32	18,700	1.84	
1.53	56.6	0.83	20,900	2.12	
2.63	72.5	1.29	16,300	2.20	
3.50	94.7	2.94	25,800	2.66	
4.57	88.3	2.14	13,000	2.64	
5.68	94.2	2.84	12,100	3.06	37,700

#### **Example 62**

**Initiated with methyl 2 - chloropropionate:** Stock solutions were prepared with methyl acrylate (8.0 ml), CuPF<sub>6</sub> (330.7 mg), 4, 4' - di(5 - nonyl) - 2, 2' - bipyridine (725.4 mg), and methyl 2 - chloropropionate (21.2 uL). These stock solutions were transferred to glass tubes and degassed by freeze - pump - thaw. The tubes were then sealed under vacuum and heated in a 90 °C oil bath. The tubes were removed at various intervals and analyzed for conversion (GC) and molecular weight (SEC).

<b>Time (hr)</b>	<b>Conversion (%)</b>	<b>ln [M]<sub>0</sub>/[M]</b>	<b>M<sub>n</sub></b>	<b>M<sub>w</sub> / M<sub>n</sub></b>	<b>M<sub>n</sub> theo</b>
0.33	53.0	0.76	38,200	1.34	
0.70	90.6	2.37	36,400	1.99	
1.25	>99	4.61	41,200	2.22	40,000

### Example 63

**Initiated with methyl 2 - bromopropionate:** Stock solutions were prepared with methyl acrylate (8.0 ml),  $\text{CuPF}_6$  (167.2 mg), 4, 4' - di(5 - nonyl) - 2, 2' - bipyridine (363.1 mg), and methyl 2 - bromopropionate (21.3  $\mu\text{L}$ ). Upon addition of the methyl 2 - bromopropionate, the reaction became exothermic and the contents of the flask became solid within ten minutes. The contents were analyzed for molecular weight (SEC), Final  $M_n=61,500$ ,  $M_w / M_n=1.62$ .

### Example 64

**Initiated with methyl 2 -iodopropionate:** Stock solutions were prepared with methyl acrylate (8.0 ml),  $\text{CuPF}_6$  (167.2 mg), 4, 4' - di(5 - nonyl) - 2, 2' - bipyridine (363.1 mg), and methyl 2 - iodopropionate (54.3  $\mu\text{L}$ ). Upon addition of the methyl 2 - iodopropionate, the reaction became exothermic and the contents of the flask became solid within ten minutes. The contents were analyzed for molecular weight (SEC), Final  $M_n=42,000$ ,  $M_w / M_n=1.75$ .

### Example 65

**Polymerization with  $\text{CuPF}_6$  /  $\text{CuBr}$ :** Stock solutions were prepared with methyl acrylate (8.0 ml),  $\text{CuPF}_6$  (33.1 mg), 4, 4' - di(5 - nonyl) - 2, 2' - bipyridine (81.4 mg), copper (I) bromide (1.3 mg) and methyl 2 - bromopropionate (22.3  $\mu\text{L}$ ). These stock solutions were transferred to glass tubes and degassed by freeze - pump - thaw. The tubes were then sealed under vacuum and heated in a 90 °C oil bath. The tubes were removed at various intervals and analyzed for conversion (GC) and molecular weight (SEC).

Time (hr)	Conversion (%)	$\ln [M]_0/[M]$	$M_n$	$M_w / M_n$	$M_n$ theo
0.38	52.7	0.75	8,600	1.62	
0.75	61.2	0.95	19,200	1.34	
1.08	96.0	3.21	33,300	1.28	

1.57	97.5	3.69	34,200	1.27	
2.03	98.4	4.12	34,100	1.32	
2.40	98.6	4.26	34,800	1.35	39,400

### Example 66

**Polymerization with  $\text{CuPF}_6$  /  $\text{CuBr}_2$ :** Stock solutions were prepared with methyl acrylate (8.0 ml),  $\text{CuPF}_6$  (33.1 mg), 4, 4' - di(5 - nonyl) - 2, 2' - bipyridine (81.4 mg), copper (II) bromide (2.0 mg) and methyl 2 - bromopropionate (22.3  $\mu\text{L}$ ). These stock solutions were transferred to glass tubes and degassed by freeze - pump - thaw. The tubes were then sealed under vacuum and heated in a 90 °C oil bath. The tubes were removed at various intervals and analyzed for conversion (GC) and molecular weight (SEC).

Time (hr)	Conversion (%)	$\ln [\text{M}]_0/[\text{M}]$	$M_n$	$M_w/M_n$	$M_n \text{ theo}$
0.17	4.9	0.05	0		
0.33	8.1	0.08	4,60	2.16	
0.50	17.0	0.19	4,700	1.41	
0.67	6.4	0.06	6,900	1.29	
0.83	26.1	0.30	9,500	1.20	10,500

### Methyl Methacrylate

### Example 67

**Initiated with p - toluenesulfonyl chloride:** Stock solutions were prepared with methyl methacrylate (8.0 ml),  $\text{CuPF}_6$  (39.0 mg), 4, 4' - di(5 - nonyl) - 2, 2' - bipyridine (152.6 mg), and p - toluenesulfonyl chloride (71.3 mg). These stock solutions were transferred to glass tubes and degassed by freeze - pump - thaw. The tubes were then sealed under vacuum and heated in a 90 °C oil bath. The tubes were removed at various intervals and analyzed for conversion (GC) and molecular weight (SEC).

Time (hr)	Conversion (%)	$\ln [M_0/M]$	$M_n$	$M_w/M_n$	$M_n$ theo
0.50	46.7	0.27	11,500	1.35	
1.05	62.1	0.42	17,100	1.19	
1.50	72.0	0.55	22,300	1.11	
2.00	77.9	0.66	22,400	1.17	
2.50	88.7	0.95	26,100	1.16	19,000

### Carboxylates ( $RCOO^-$ )

#### Example 68

**Comparitive Polymerization using CuBr / 4,4'-di(5-nonyl)-2,2'-bipyridine :** The following reagents were transferred into glass tubes purged with argon: 12.6 mg ( $8.73 \times 10^{-2}$  mmol) of CuBr, 1.0 ml (8.73 mmol) of styrene, 12.0 ml ( $8.73 \times 10^{-2}$  mmol) of 1-phenylethyl bromide and 71.2 mg ( $17.5 \times 10^{-2}$  mmol) of 4,4'-di(5-nonyl)-2,2'-bipyridine . Each tube was degassed three times by "freeze-pump-thaw" cycles and sealed under vacuum. The tubes were placed in an oil bath thermostated at 90 °C and were removed from the oil bath at timed intervals.

Sample	Time(hr)	Conversion (%)	$M_n$ (th.)	$M_n$ (GPC)	$M_w/M_n$
1	1.5	11.4	1,200	2,200	1.13
2	3.0	31.2	3,200	3,100	1.15
3	4.5	43.3	4,500	4,000	1.15
4	6.0	48.2	5,000	5,000	1.10

### Acetate

#### Example 69

##### Bulk Polymerization of Styrene using two 4,4'-di(5-nonyl)-2,2'-bipyridine / CuOAc:

The following reagents were transferred into glass tubes purged with argon: 10.7 mg ( $8.73 \times$

$10^{-2}$  mmol) of CuOAc, 1.0 ml (8.73 mmol) of styrene, 12.0 ml ( $8.73 \times 10^{-2}$  mmol) of 1-phenylethyl bromide and 71.2 mg ( $17.5 \times 10^{-2}$  mmol) of 4,4'-di(5-nonyl)-2,2'-bipyridine. Each tube was degassed three times by "freeze-pump-thaw" cycles and sealed under vacuum. The tubes were placed in an oil bath thermostated at 90 °C and were removed from the oil bath at timed intervals.

<u>Sample</u>	<u>Time(hr)</u>	<u>Conversio n (%)</u>	<u>M<sub>n</sub>(th.)</u>	<u>M<sub>n</sub>(GPC)</u>	<u>M<sub>w</sub> / M<sub>n</sub></u>
1	1.0	37.1	3,900	5,500	1.34
2	2.0	57.6	6,000	10,100	1.20
3	3.0	83.3	8,700	13,500	1.49

#### Example 70

##### **Bulk Polymerization of Styrene using one 4,4'-di(5-nonyl)-2,2'-bipyridine / CuOAc:**

The following reagents were transferred into glass tubes purged with argon: 10.7 mg ( $8.73 \times 10^{-2}$  mmol) of CuOAc, 1.0 ml (8.73 mmol) of styrene, 12.0 ml ( $8.73 \times 10^{-2}$  mmol) of 1-phenylethyl bromide and 35.6 mg ( $8.73 \times 10^{-2}$  mmol) of 4,4'-di(5-nonyl)-2,2'-bipyridine. Each tube was degassed three times by "freeze-pump-thaw" cycles and sealed under vacuum. The tubes were placed in an oil bath thermostated at 90 °C and were removed from the oil bath at timed intervals.

<u>Sample</u>	<u>Time (h)</u>	<u>Conversio n (%)</u>	<u>M<sub>n</sub>(th)</u>	<u>M<sub>n</sub>(SEC)</u>	<u>M<sub>w</sub> / M<sub>n</sub></u>
1	1.0	26.4	2,700	3,300	1.54
2	2.0	52.8	5,500	7,200	1.24
3	3.0	74.0	7,700	8,500	1.33
4	4.0	92.8	9,700	11,500	1.44

### Example 71

#### Bulk Polymerization of Styrene using 0.5 CuBr / 2 4,4'-di(5-nonyl)-2,2'-bipyridine /

**0.5CuOAc:** The following reagents were transferred into glass tubes purged with argon: 5.5 mg ( $4.36 \times 10^{-2}$  mmol) of CuOAc, 6.3 mg ( $4.36 \times 10^{-2}$  mmol) of CuBr, 1.0 ml (8.73 mmol) of styrene, 12.0 ml ( $8.73 \times 10^{-2}$  mmol) of 1-phenylethyl bromide and 71.2 mg ( $17.5 \times 10^{-2}$  mmol) of 4,4'-di(5-nonyl)-2,2'-bipyridine. Each tube was degassed three times by "freeze-pump-thaw" cycles and sealed under vacuum. The tubes were placed in an oil bath thermostated at 90 °C and were removed from the oil bath at timed intervals.

<u>Sample</u>	<u>Time(hr)</u>	<u>Conversio n (%)</u>	<u>M<sub>n</sub>(th.)</u>	<u>M<sub>n</sub>(GPC)</u>	<u>M<sub>w</sub> / M<sub>n</sub></u>
1	1.0	16.8	1,700	2,500	1.23
2	2.0	32.4	3,400	4,500	1.15
3	3.0	50.7	5,300	6,300	1.14
4	4.0	58.9	6,100	7,900	1.24

### Example 72

#### Bulk Polymerization of Styrene using 0.1CuBr<sub>2</sub> / 2.2 4,4'-di(5-nonyl)-2,2'-bipyridine /

**CuOAc:** The following reagents were transferred into glass tubes purged with argon: 10.7 mg ( $8.73 \times 10^{-2}$  mmol) of CuOAc, 2.0 mg ( $0.87 \times 10^{-2}$  mmol) of CuBr<sub>2</sub>, 1.0 ml (8.73 mmol) of styrene, 12.0 ml ( $8.73 \times 10^{-2}$  mmol) of 1-phenylethyl bromide and 78.3 mg ( $19.2 \times 10^{-2}$  mmol) of 4,4'-di(5-nonyl)-2,2'-bipyridine. Each tube was degassed three times by "freeze-pump-thaw" cycles and sealed under vacuum. The tubes were placed in an oil bath thermostated at 90 °C and were removed from the oil bath at timed intervals.

<u>Sample</u>	<u>Time(hr)</u>	<u>Conversoi n (%)</u>	<u>M<sub>n</sub>(th.)</u>	<u>M<sub>n</sub>(GPC)</u>	<u>M<sub>w</sub> / M<sub>n</sub></u>
1	1.0	27.5	2,900	3,200	1.34
2	2.0	46.6	4,800	6,200	1.18

3	3.0	66.5	6,900	8,700	1.18
4	5.0	90.3	9,400	11,500	1.24

## 2 - Thiophenecarboxylate

Copper (I) 2 - thiophenecarboxylate (CuTc) was prepared according to G. D. Allred, L. S. Liebeskind *J. Amer. Chem. Soc.* (1996) **118**, 2748

### **Example 73**

**Bulk Polymerization of Styrene using two 4,4'-di(5-nonyl)-2,2'-bipyridine / CuTc:** The following reagents were transferred into glass tubes purged with argon: 16.6 mg ( $8.73 \times 10^{-2}$  mmol) of copper (I) 2 - thiophenecarboxylate (CuTc), 1.0 ml (8.73 mmol) of styrene, 12.0 ml ( $8.73 \times 10^{-2}$  mmol) of 1-phenylethyl bromide and 71.2 mg ( $17.5 \times 10^{-2}$  mmol) of 4,4'-di(5-nonyl)-2,2'-bipyridine . Each tube was degassed three times by "freeze-pump-thaw" cycles and sealed under vacuum. The tubes were placed in an oil bath thermostated at 90 °C and were removed from the oil bath at timed intervals.

<b>Sample</b>	<b>Time(hr)</b>	<b>Conversio n (%)</b>	<b>M<sub>n</sub>(th.)</b>	<b>M<sub>n</sub>(GPC)</b>	<b>M<sub>w</sub> / M<sub>n</sub></b>
1	1.0	22.7	2,400	2,600	1.56
2	2.0	35.5	3,700	5,000	1.21
3	4.0	44.8	4,700	7,400	1.18
4	6.0	58.0	6,000	9,300	1.20

### **Example 74:**

**Bulk Polymerization of Styrene using 4,4'-di(5-nonyl)-2,2'-bipyridine / CuTc:** The following reagents were transferred into glass tubes purged with argon: 16.6 mg ( $8.73 \times 10^{-2}$  mmol) of copper (I) 2 - thiophenecarboxylate, 1.0 ml (8.73 mmol) of styrene, 12.0 ml ( $8.73 \times 10^{-2}$  mmol) of 1-phenylethyl bromide and 35.6 mg ( $8.73 \times 10^{-2}$  mmol) of 4,4'-di(5-nonyl)-2,2'-bipyridine . Each tube was degassed three times by "freeze-pump-thaw" cycles and sealed under vacuum. The

tubes were placed in an oil bath thermostated at 90 °C and were removed from the oil bath at timed intervals.

Sample	Time(hr)	Conversion n (%)	M <sub>n</sub> (th.)	M <sub>n</sub> (GPC)	M <sub>w</sub> / M <sub>n</sub>
1	1.0	20.0	2,100	3,500	1.33
2	2.0	35.0	3,600	5,100	1.23
3	4.0	51.9	5,400	7,400	1.18
4	6.0	67.0	7,000	9,900	1.23

### R-X / CuY

#### **Example 75**

**Solution Polymerization of Methyl Methacrylate / 1 - Phenylethyl Chloride / CuCl:** A dry round-bottomed flask was charged with CuCl (23.2 mg; 0.234 mmol), 4, 4' - di(5-nonyl) - 2,2' - bipyridine (190.9 mg; 0.468 mmol) and diphenyl ether (10.0 ml). The flask was sealed with a rubber septum and was cycled between vacuum and argon three times to remove the oxygen. Degassed methyl methacrylate (10.0 ml; 93.6 mmol) was added using degassed syringes and stainless steel needles. The 1-phenylethyl chloride (62 mL; 0.468 mmol) was added and the flask was immersed in an oil bath held by a thermostat at 90 °C. At various times samples were taken via syringe to monitor conversion (GC) and molecular weight (SEC).

Time (h)	Conversion (%)	M <sub>n</sub> (th.)	M <sub>n</sub> (SEC)	M <sub>w</sub> / M <sub>n</sub>
1.0	31	6200	26400	3.34
2.0	59	11800	33100	3.20
3.0	62	12400	35000	2.80
4.0	77	15400	38400	2.40
20.0	95	19000	32200	2.60

#### **Example 76**

**Solution Polymerization of Methyl Methacrylate / 1 - Phenylethyl Chloride / CuBr:** A dry round-bottomed flask was charged with CuBr (34.0 mg; 0.234 mmol), 4, 4' - di(5-nonyl) - 2,2' -

bipyridine (190.9 mg; 0.468 mmol) and diphenyl ether (10.0 ml). The flask was sealed with a rubber septum and was cycled between vacuum and argon three times to remove the oxygen. Degassed methyl methacrylate (10.0 ml; 93.6 mmol) was added using degassed syringes and stainless steel needles. The 1-phenylethyl chloride (62 mL; 0.468 mmol) was added and the flask was immersed in an oil bath held by a thermostat at 90 °C. At various times samples were taken via syringe to monitor conversion (GC) and molecular weight (SEC).

<u>Time (h)</u>	<u>Conversion (%)</u>	<u>M<sub>n</sub>,<sub>th</sub></u>	<u>M<sub>n</sub>,<sub>SEC</sub></u>	<u>M<sub>w</sub> / M<sub>n</sub></u>
1.0	28	5600	96000	2.95
2.0	53	10600	105000	2.77
3.0	62	12400	98000	2.95
16.0	93	18600	76000	3.22

### Example 77

**Solution Polymerization of Methyl Methacrylate / 1 - Phenylethyl Bromide / CuCl:** A dry round-bottomed flask was charged with CuCl (23.2 mg; 0.234 mmol), 4, 4' - di(5-nonyl) - 2,2' - bipyridine (190.9 mg; 0.468 mmol) and diphenyl ether (10.0 ml). The flask was sealed with a rubber septum and was cycled between vacuum and argon three times to remove the oxygen. Degassed methyl methacrylate (10.0 ml; 93.6 mmol) was added using degassed syringes and stainless steel needles. The 1-phenylethyl bromide (64 mL; 0.468 mmol) was added and the flask was immersed in an oil bath held by a thermostat at 90 °C. At various times samples were taken via syringe to monitor conversion (GC) and molecular weight (SEC).

<u>Time (h)</u>	<u>Conversion (%)</u>	<u>M<sub>n</sub>,<sub>th</sub></u>	<u>M<sub>n</sub>,<sub>SEC</sub></u>	<u>M<sub>w</sub> / M<sub>n</sub></u>
1.0	55	11000	15800	1.31
2.0	63	12600	18600	1.30
3.0	72	14400	21000	1.29
21.0	97	19400	22200	1.28

## Effect of Solvent on ATRP

### **Example 78**

**Solution Polymerization of n-Butyl Acrylate in Diphenyl Ether (Initiator = 1 - Phenylethyl Bromide):** A dry round-bottomed flask was charged with CuBr (0.250 g;  $1.74 \times 10^{-3}$  mol), 2,2'-bipyridyl (0.816 g;  $5.23 \times 10^{-3}$  mol) and diphenyl ether (10.0 ml). The flask was sealed with a rubber septum and was cycled between vacuum and argon three times to remove the oxygen. Degassed *n*-butyl acrylate (10.0 ml;  $6.98 \times 10^{-2}$  mol) was added using degassed syringes and stainless steel needles. The 1-phenylethyl bromide (0.238 ml;  $1.74 \times 10^{-3}$  mol) was added and the flask was immersed in an oil bath held by a thermostat at 100 °C. After 65 min, the conversion of *n*-butyl acrylate was 42%. After 480 min, the conversion was 95%, and the produced poly(*n*-butyl acrylate) had  $M_n = 5100$  and  $M_w/M_n = 1.87$ .

### **Example 79**

**Solution Polymerization of n-Butyl Acrylate in Benzene (Initiator = 1 - Phenylethyl Bromide):** A dry round-bottomed flask was charged with CuBr (0.250 g;  $1.74 \times 10^{-3}$  mol) and 2,2'-bipyridyl (0.816 g;  $5.23 \times 10^{-3}$  mol). The flask was sealed with a rubber septum and was cycled between vacuum and argon three times to remove the oxygen. Degassed *n*-butyl acrylate (10.0 ml;  $6.98 \times 10^{-2}$  mol) and unhydrous benzene (10.0 ml) was added using degassed syringes and stainless steel needles. The methyl 2-bromopropionate (0.194 ml;  $1.74 \times 10^{-3}$  mol) was added and the flask was immersed in an oil bath held by a thermostat at 80 °C. After 100 min, the conversion of *n*-butyl acrylate was 9%. After 4380 min, the conversion was 72%, and the produced poly(*n*-butyl acrylate) had  $M_n = 9100$  and  $M_w/M_n = 2.42$ .

### **Example 80**

**Solution Polymerization of n-Butyl Acrylate in Propylene Carbonate (Initiator = 1 - Phenylethyl Bromide):** A dry round-bottomed flask was charged with CuBr (0.250 g;  $1.74 \times 10^{-3}$  mol), 2,2'-bipyridyl (0.816 g;  $5.23 \times 10^{-3}$  mol) and propylene carbonate (10.0 ml). The flask was sealed with a rubber septum and was cycled between vacuum and argon three

times to remove the oxygen. Degassed *n*-butyl acrylate (10.0 ml;  $6.98 \times 10^{-2}$  mol) was added using degassed syringes and stainless steel needles. The 1-phenylethyl bromide (0.238 ml;  $1.74 \times 10^{-3}$  mol) was added and the flask was immersed in an oil bath held by a thermostat at 100 °C. After 60 min, the conversion of *n*-butyl acrylate was 49%. After 480 min, the conversion was 94%, and the produced poly(*n*-butyl acrylate) had  $M_n = 4700$  and  $M_w/M_n = 1.27$ .

### **Example 81**

**Solution Polymerization of *n*-Butyl Acrylate in Ethylene Carbonate (Initiator = Methyl 2 - Bromopropionate):** A dry round-bottomed flask was charged with CuBr (0.250 g;  $1.74 \times 10^{-3}$  mol), 2,2'-bipyridyl (0.816 g;  $5.23 \times 10^{-3}$  mol) and ethylene carbonate (10.0 g). The flask was sealed with a rubber septum and was heated to melt the ethylene carbonate, and was cycled between vacuum and argon three times to remove the oxygen. Degassed *n*-butyl acrylate (10.0 ml;  $6.98 \times 10^{-2}$  mol) was added using degassed syringes and stainless steel needles. The methyl 2-bromopropionate (0.194 ml;  $1.74 \times 10^{-3}$  mol) was added and the flask was immersed in an oil bath held by a thermostat at 100 °C. After 60 min, the conversion of *n*-butyl acrylate was 97%, and the produced poly(*n*-butyl acrylate) had  $M_n = 5400$  and  $M_w/M_n = 1.23$ .

### **Example 82**

**Solution Polymerization of *n*-Butyl Acrylate in Ethylene Carbonate (Initiator = 1 - Phenylethyl Bromide):** A dry round-bottomed flask was charged with CuBr (0.250 g;  $1.74 \times 10^{-3}$  mol), 2,2'-bipyridyl (0.816 g;  $5.23 \times 10^{-3}$  mol) and ethylene carbonate (10.0 g). The flask was sealed with a rubber septum and was heated to melt the ethylene carbonate, and was cycled between vacuum and argon three times to remove the oxygen. Degassed *n*-butyl acrylate (10.0 ml;  $6.98 \times 10^{-2}$  mol) was added using degassed syringes and stainless steel needles. The 1-phenylethyl bromide (0.238 ml;  $1.74 \times 10^{-3}$  mol) was added and the flask was immersed in an oil bath held by a thermostat at 100 °C. After 60 min, the conversion of *n*-butyl acrylate was 99%, and the produced poly(*n*-butyl acrylate) had  $M_n = 5000$  and  $M_w/M_n = 1.36$ .

## Effect of CuBr on Conventional Free Radical Polymerization

### **Acrylonitrile**

#### **Example 83**

**Polymerization of Acrylonitrile with AIBN:** 25.0g ( 0.284 mol ) of ethylene carbonate and 0.0249g (  $1.52 \times 10^{-4}$  mol ) AIBN were put into a schlenk flask under argon. 10.0 ml (0.152 mol) of degassed acrylonitrile was added to the flask via syringe and then the flask was placed into an oil bath thermostated at 64 °C. 4ml samples were removed at certain time intervals. 3ml of the sample was dissolved in 6ml THF for GC analysis and 1ml in DMF for GPC measurement. The conversion was determined with GC and the molecular weight and molecular weight distribution were obtained from GPC using polystyrene standards.

Time (hour)	Conversion	$\ln([M]_0/[M])$	$M_w$ (GPC)	$M_w/M_n$
0.75	86.1	0.09	178,700	3.47
1.5	22.0	0.25	425,200	1.54
3.25	62.5	0.98	495,300	1.53

#### **Example 84**

**Polymerization of Acrylonitrile with AIBN, and CuBr / Bipyridine:** 25.0g ( 0.284mol ) of ethylene carbonate , 0.0249g (  $1.52 \times 10^{-4}$  mol ) AIBN, 0.0434g, (  $3.04 \times 10^{-4}$  mol ) CuBr and 0.0949g (  $6.08 \times 10^{-4}$  mol ) 2,2'-bipyridine were put into a schlenk flask under argon. 10.0 ml (0.152 mol ) of degassed acrylonitrile was added to the flask via syringe and the flask was then placed into an oil bath thermostated at 64 °C. 4ml samples were taken at certain time intervals. 3ml of the sample dissolved in 6ml THF for GC and 1ml in DMF for GPC measurement. The conversion was determined with GC and the molecular weight and molecular weight distribution were obtained from GPC using polystyrene standards.

Time (hour)	Conversion	ln([M] <sub>0</sub> /[M])	M <sub>w</sub> (GPC)	M <sub>w</sub> / M <sub>n</sub>
1	3.4	0.04	NA	NA
3	6.5	0.07	60,200	1.53
5	12.6	0.13	69,800	1.46
8	16.3	0.18	86,900	1.33
10	28.3	0.33	74,400	1.51
21.5	42.1	0.55	79,700	1.58
46	54.0	0.78	80,400	1.58

### Methyl Acrylate

#### Example 85

**Polymerization of Methyl Acrylate with AIBN:** 0.0728 g (  $4.43 \times 10^{-4}$  mol ) AIBN were put into a schlenk flask under argon. 10 ml degassed toluene and 4 ml (  $4.43 \times 10^{-2}$  mol ) degassed methyl acrylate were added to the flask via syringe and the flask was then placed into an oil bath thermostated at 50 °C. 0.5 ml samples were taken at certain time intervals and dissolved in 1 ml THF. The conversion was determined with GC and the molecular weight and molecular weight distribution were obtained from GPC using polystyrene standards.

Time (hour)	Conversion	$\ln([M]_0/[M])$	$M_w$ (GPC)	$M_w/M_n$
1.0	33.7	0.41	$1.00 \times 10^5$	2.48
1.5	49.4	0.68	75,500	2.80
2.0	55.2	0.80	71,700	2.89
3.25	71.4	1.25	42,900	3.73
5.0	76.9	1.46	31,900	4.20

### Example 86

**Polymerization of Methylacrylate with AIBN and CuBr / Bipyridine:** 0.0728 g (  $4.43 \times 10^{-4}$  mol ) AIBN, 0.1274 g (  $8.87 \times 10^{-4}$  mol ) CuBr and 4,4'-di(5-nonyl)-2,2'-bipyridine (  $1.77 \times 10^{-3}$  mol ) were added to a schlenk flask under argon. 10 ml degassed toluene and 4 ml (  $4.43 \times 10^{-2}$  mol ) degassed methyl acrylate were added to the flask via syringe and the flask was then placed into an oil bath thermostated at 50 °C. 0.5 ml samples were removed at certain time intervals and dissolved in 1 ml THF. The conversion was determined with GC and the molecular weight and molecular weight distribution were obtained from GPC using polystyrene standards.

Time (hour)	Conversion	$\ln([M]_0/[M])$	$M_w$ (GPC)	$M_w/M_n$
3.833	7.3	0.08	21,800	1.36
6.333	20.0	0.22	34,400	1.51
9.000	31.1	0.37	36,000	1.62
18.10	59.1	0.90	30,300	1.93
28.25	74.5	1.36	21,800	2.22
45.42	86.4	2.00	18,207	2.37

### Reverse ATRP

#### Styrene

### Example 87

**Bulk Polymerization of Styrene by Reverse ATRP:** Tubes were prepared in the following manner.  $\text{CuBr}_2$  (11.2 mg, 0.05 mmol) and 4, 4' - di -(5 - nonyl) - 2, 2' - bipyridine (40.8 mg, 0.1 mmol) were added to a dry glass tube. A 1.0 ml solution of AIBN (0.057 M) in styrene was added to the tube. The contents of the tube were degassed by the "freeze - pump - thaw" method and then sealed under vacuum. The tubes were then placed in a 50 °C oil bath until a homogeneous solution was obtained (30 min.). The tubes were then placed in a 110 °C oil bath and removed at various time intervals. Conversion was determined by GC, and molecular weights were determined by SEC analysis.

Sample	Time (h)	Conversion(%)	$M_n$ , Cal	$M_n$ , SEC	$M_w/M_n$
1	1.0	18.9	1,500	2,100	1.13
2	2.0	35.9	2,900	3,900	1.09
3	4.5	55.7	4,500	5,300	1.08
4	7.0	72.6	5,800	7,300	1.09

### Methyl Acrylate

### Example 88

**Solution Polymerization of Methyl Acrylate by Reverse ATRP:** To a 25 ml round bottom flask, with a magnetic stir bar,  $\text{CuBr}_2$  (50.2 mg, 0.225 mmol) and 4, 4' - di -(5 - nonyl) - 2, 2' - bipyridine (183.6 mg, 0.45 mmol) were added. The flask was sealed with a rubber septum and the contents degassed by applying a vacuum and backfilling with argon. Degassed methyl acrylate (4.5 ml) and anisole (5.0 ml) were added via syringe. The contents were placed in an oil bath at 110 °C and stirred until the contents dissolved. AIBN (44.3 mg, 0.27 mmol) was then added as a solution in a small amount of methyl acrylate (0.5 ml). The reaction mixture was stirred at 110 °C and samples were taken at various time intervals to monitor conversion (GC) and molecular weight (SEC).

Sample	Time (h)	Conversion(%)	$M_n$ , Cal	$M_n$ , SEC	$M_w/M_n$
1	1.0	34.0	3,000	3,100	1.15

2	2.0	52.0	4,700	5,300	1.10
3	3.0	68.9	6,200	6,500	1.09
4	4.0	76.2	6,800	6,900	1.09
5	5.3	83.2	7,400	7,600	1.09
6	6.8	87.4	7,800	7,800	1.10
7	10.2	89.6	8,000	8,300	1.11

### **Methyl Methacrylate**

#### **Example 89**

**Solution Polymerization of Methyl Methacrylate by Reverse ATRP:** To a 25 ml round bottom flask, with a magnetic stir bar,  $\text{CuBr}_2$  (25.7 mg, 0.115 mmol) and 4, 4' - di -(5 - nonyl) - 2, 2' - bipyridine (93.8 mg, 0.23 mmol) were added. The flask was sealed with a rubber septum and the contents degassed by applying a vacuum and backfilling with argon. Degassed methyl methacrylate (4.5 ml) and anisole (5.0 ml) were added via syringe. The contents were placed in an oil bath at 90 °C and stirred until the contents dissolved. AIBN (19.7 mg, 0.12 mmol) was then added as a solution in a small amount of methyl methacrylate (0.5 ml). The reaction mixture was stirred at 90 °C and samples were taken at various time intervals to monitor conversion (GC) and molecular weight (SEC).

Sample	Time (h)	Conversion (%)	Mn, Cal	Mn, SEC	Mw/Mn
1	1.48	17.6	3,500	2,600	1.12
2	2.12	30.4	6,100	8,700	1.07
3	2.75	45.4	9,100	12,500	1.10
4	3.27	56.3	11,300	13,700	1.14
5	3.83	62.7	12,500	15,200	1.15
6	4.42	66.1	13,200	16,500	1.17
7	5.50	74.0	14,800	17,600	1.20

### Acrylonitrile

#### Example 90

**Polymerization of Acrylonitrile with AIBN, and CuBr<sub>2</sub> /Bipyridine:** 25.0 g ( 0.284mol ) of ethylene carbonate , 0.0249 g (  $1.52 \times 10^{-4}$  mol ) AIBN, 0.06107 g (  $2.73 \times 10^{-4}$  mol ) CuBr<sub>2</sub> and 0.0949 g (  $5.47 \times 10^{-4}$  mol ) 2,2'-bipyridine were added to a schlenk flask under argon. 10.0 ml (0.152 mol) degassed acrylonitrile was added to the flask via syringe and the flask was then placed into an oil bath thermostated at 64 °C. 4 ml samples were removed at certain time intervals. 3 ml of the sample was dissolved in 6ml of THF for GC and 1 ml in DMF for GPC measurement. Conversion was determined with GC and the molecular weight and molecular weight distribution were obtained from GPC using polystyrene standards.

Time (hour)	Conversion	ln([M] <sub>0</sub> /[M])	M <sub>w</sub> (GPC)	M <sub>w</sub> /M <sub>n</sub>
2.0	0	0	NA	NA
8.5	7.1	0.07	19,700	1.20
10	10.6	0.11	33,500	1.11
22	26.6	0.31	74,800	1.29
46	37.0	0.46	93,100	1.22

## Acrylic Polymers by ATRP

### **Example 91**

**Homogeneous ATRP of Vinyl Acrylate** The following amounts of reagents were weighed into a glass tube under ambient temperature: 12mg ( $8.37 \times 10^{-2}$  mmol) of CuBr, 1.00 mL (0.942 g, 9.42 mmol) of vinyl acrylate, 60 mg (0.175 mmol) 4,4'-Di-(5-nonyl)-2,2'-bipyridine, and 36 mL ( $27 \times 10^{-2}$  mmol) 2-methylbromopropionate. Two “freeze-pump-thaw” cycles were performed on the contents of the tube to insure that oxygen was removed from the polymerization solution. The tube was sealed under vacuum and placed in an oil bath thermostated at 60 °C. After 10h, the tube was broken, and the contents were dissolved in 10 mL of THF. Conversion of the sample was measured using GC, and the molecular weight and polydispersity were determined by GPC. Conversion was 97 %,  $M_n = 2800$ ,  $M_w/M_n = 1.21$ . The  $^1\text{H}$  NMR spectrum confirmed that the vinyl group remained unaffected, and that the polymerization involves acrylic unsaturation of monomer.

### **Example 92**

**Homogeneous ATRP of Allyl Acrylate** The following amounts of reagents were weighed into a glass tube under ambient temperature: 12mg ( $8.37 \times 10^{-2}$  mmol) of CuBr, 1.00 mL (1 g, 9 mmol) of allyl acrylate, 60 mg (0.175 mmol) 4,4'-Di-(5-nonyl)-2,2'-bipyridine, and 36 mL ( $27 \times 10^{-2}$  mmol) methyl 2 - bromopropionate. Two “freeze-pump-thaw” cycles were performed on the contents of the tube in order to insure that oxygen was removed from the polymerization solution. The tube was sealed under vacuum and placed in an oil bath thermostated at 30 °C. After 15 min, the tube was broken, and the contents were dissolved in 10 mL of THF. Conversion of the monomer was measured using GC. Conversion was 97 %, and the polymer was an insoluble gel.

### **Example 93**

**Homogeneous ATRP of t-Butyl Acrylate:** The following amounts of reagents were weighed into glass tubes under ambient temperature: 12mg ( $8.37 \times 10^{-2}$  mmol) of CuBr, 1.00 mL (0.872 g, 6.8 mmol) of t-butyl acrylate, 60 mg (0.175 mmol) 4,4'-di-(5-nonyl)-2,2'-bipyridine, and 22 mL ( $17 \times 10^{-2}$  mmol) methyl 2 - bromopropionate. Two “freeze-pump-thaw” cycles were performed

on the contents of each tube to insure that oxygen was removed from the polymerization solution. The tubes were sealed under vacuum and placed in an oil bath thermostated at 90 °C. At various time intervals the tubes were removed from the oil bath and cooled to 0 °C to quench the polymerization. Afterwards, the individual tubes were broken, and the contents dissolved in 10 mL of THF. Conversion of the samples was measured using GC, and the molecular weight and polydispersities were measured by GPC. The resulting poly(t-butyl acrylate) was subsequently hydrolysed in the presence of 1% of p-toluenesulfonic acid (in THF) to poly(acrylic acid).

<u>Time (h)</u>	<u>Conversion (%)</u>	<u>M<sub>n</sub></u>	<u>M<sub>w</sub>/M<sub>n</sub></u>
3	27	11200	1.22
7	44	18600	1.21
12	57	24200	1.21
16	80	33500	1.20
20	98	41300	1.19

#### **Example 94**

**Homogeneous ATRP of Isobornyl Acrylate** The following amounts of reagents were weighed into glass tubes under ambient temperature: 12mg (8.37x10<sup>-2</sup> mmol) of CuBr, 1.00 mL (0.986 g, 4.78 mmol) of isobornyl acrylate, 60 mg (0.175 mmol) 4,4'-di-(5-nonyl)-2,2'-bipyridine, and 27 mL (20x10<sup>-2</sup> mmol) 2-methylbromopropionate. Two "freeze-pump-thaw" cycles were performed on the contents of each tube to insure that oxygen was removed from the polymerization solutions. Each tube was sealed under vacuum and placed in an oil bath thermostated at 90 °C. At time intervals the tubes were removed from the oil bath and cooled to 0°C in order to quench the polymerization. Afterwards, the individual tubes were broken, and the contents dissolved in 10 mL of THF. Conversion of the monomer was measured using GC, and the molecular weight and polydispersities were measured by GPC.

<u>Time (h)</u>	<u>Conversion (%)</u>	<u>M<sub>n</sub></u>	<u>M<sub>w</sub>/M<sub>n</sub></u>
0.5	10	1000	1.31
1	28	1540	1.25
2	73	3280	1.21
2.5	81	3720	1.15

**Example 95**

**Copolymerization of Butyl Acrylate and 3 - (Trimethoxysilyl)propyl Methacrylate:** The following reagents were weighed into a round bottom flask under ambient temperature: 510 mg (3.5 mmol) of CuBr, 33.2 mL (34.65 g, 8.62 mmol) of 3 - (trimethoxysilyl)propyl methacrylate, 1.64 g (10.5 mmol) of 2,2'-bipyridine, 80.0 ml (71.52 g, 558 mmol) of butyl acrylate and 3.89 mL (34.9 mmol) methyl 2-bromopropionate. The flask was sealed with a rubber septum and the contents of the flask were degassed by sparging with argon. The reaction was heated to 100 °C and stirred. After 18h the reaction was quenched by pouring into dichloromethane. Conversion of the monomer was measured using  $^1\text{H}$  NMR, conversion > 95 %. The copper was removed by passing through alumina and the solvent removed under vacuum. The  $^1\text{H}$  NMR spectrum confirmed that the trimethylsilyl groups remained, and that the polymerization involved only the methacrylic unsaturation of monomer. Upon exposure to air (ambient moisture), the polymer gelled as a result of reaction between the trimethylsilyl groups and water.

**Example 96**

**Homogeneous ATRP of Glycidyl Acrylate:** The following amounts of reagents were weighed into glass tubes under ambient temperature: 3mg ( $2.1 \times 10^{-2}$  mmol) of CuBr, 1.00 mL (1.1 g, 8.59 mmol) of glycidyl acrylate, 15 mg ( $4.2 \times 10^{-2}$  mmol) 4,4'-di-(5-nonyl)-2,2'-bipyridine, and 5 mL ( $4 \times 10^{-2}$  mmol) methyl 2-bromopropionate. Two "freeze-pump-thaw" cycles were performed on the contents of each tube to insure that oxygen was removed from the polymerization solution. Each tube was sealed under vacuum and placed in an oil bath thermostated at 90 °C. At various time intervals the tubes were removed from the oil bath and cooled to 0 °C in order to quench the polymerization. Afterwards, the individual tubes were broken, and the contents were dissolved in 10 mL of THF. Conversion of the monomer was measured using GC, and the molecular weight and polydispersity were measured by GPC. A  $^1\text{H}$  NMR study revealed that the oxirane ring remained unchanged, and that the polymerization involved exclusively the acrylic unsaturation of the monomer.

Time, min	Conversion, %	M <sub>n</sub>	M <sub>w</sub> /M <sub>n</sub>
15	51.5	13600	1.40
30	69.2	17890	1.38
45	82.5	21200	1.28
60	91.2	23400	1.21
90	98.0	25200	1.21

### **Water Soluble Acrylic Polymers**

#### **Example 97**

**Homogeneous ATRP of 2-hydroxyethyl acrylate:** The following amounts of reagents were weighed into glass tubes under ambient temperature: 12mg ( $8.37 \times 10^{-2}$  mmol) of CuBr, 1.00 mL (1.01 g, 8.62 mmol) of 2-hydroxyethyl acrylate, 60 mg (0.175 mmol) 4,4'-di-(5-nonyl)-2,2'-bipyridine, and 18 mL ( $14 \times 10^{-2}$  mmol) methyl 2-bromopropionate. Two “freeze-pump-thaw” cycles were performed on the contents of each tube in order to insure that oxygen was removed from the polymerization solution. Each tube was sealed under vacuum. The tubes were placed in an oil bath thermostated at 90 °C. At various time intervals the tubes were removed from the oil bath and cooled to 0 °C to quench the polymerization. Afterwards, the individual tubes were broken, and the contents were dissolved in 10 mL of THF. Conversion of the monomer was measured using GC, and the molecular weight and polydispersity were measured by GPC. <sup>1</sup>H NMR spectra confirmed that the hydroxyl groups remained, and the polymerization involved only acrylic unsaturation of monomer.

Time, h	Conversion, %	M <sub>n</sub>	M <sub>w</sub> /M <sub>n</sub>
1	26.7	4,600	1.72
3	44.1	7,500	1.51
4	57.4	9,800	1.31
5	67.1	11,400	1.21
8	79.2	13,500	1.20
14	92.5	15,700	1.19

### **Example 98**

**Homogeneous ATRP of 2-hydroxyethyl acrylate:** The following amounts of reagents were weighed into a glass tube under ambient temperature: 12mg ( $8.37 \times 10^{-2}$  mmol) of CuBr, 1.00 mL (1.01 g, 8.62 mmol) of 2-hydroxyethyl acrylate, 60 mg (0.175 mmol) 4,4'-di-(5-nonyl)-2,2'-bipyridine, and 6 mL ( $4 \times 10^{-2}$  mmol) methyl 2-bromopropionate. Two "freeze-pump-thaw" cycles were performed on the contents of the tube to insure that oxygen was removed from the polymerization solution. The tube was sealed under vacuum and placed in an oil bath thermostated at 90 °C. The tube was broken and the contents dissolved in 10 mL of THF. Conversion of the monomer was measured using GC, and the molecular weight and polydispersity were measured by GPC. Conversion was 87 %,  $M_n = 51400$ ,  $M_w/M_n = 1.27$ . The  $^1H$  NMR spectrum confirmed that the hydroxyl groups remained, and that the polymerization involved only the acrylic unsaturation of monomer.

### **Example 99**

**Homogeneous ATRP of 2-Hydroxyethyl Acrylate in Water:** The following amounts of reagents were weighed into a glass tube under ambient temperature: 12mg ( $8.37 \times 10^{-2}$  mmol) of CuBr, 1.00 mL (1.01 g, 8.62 mmol) of 2-hydroxyethyl acrylate, 60 mg (0.175 mmol) 4,4'-di-(5-nonyl)-2,2'-bipyridine, 1mL (1g)  $H_2O$  and 18 mL ( $14 \times 10^{-2}$  mmol) methyl 2-bromopropionate. Two "freeze-pump-thaw" cycles were performed on the contents of the tube to insure that oxygen was removed from the polymerization solution. The tube was sealed under vacuum and placed in an oil bath thermostated at 90 °C. After 12 h the tube were removed from the oil bath and cooled to 0 °C in order to quench the polymerization. Afterwards, the tube was broken, and the contents were dried with  $MgSO_4$  and than dissolved in 10 mL of DMF. Conversion of the monomer was measured using GC, and the molecular weight and polydispersity were measured by GPC. The conversion was 87 %,  $M_n = 14700$ ,  $M_w/M_n = 1.34$ . The  $^1H$  NMR spectrum confirmed that the hydroxyl group remained unaffected, and the polymerization involved acrylic unsaturation of the monomer.

### **Example 100**

**Homogeneous ATRP of N-(2-Hydroxypropyl) Methacrylamide in 1-Butanol:** The following amounts of reagents were weighed into a glass tube under ambient temperature: 12mg ( $8.37 \times 10^{-2}$  mmol) of CuBr, 0.5g (3.49 mmol) of N-(2-hydroxypropyl)methacrylamide, 20 mg ( $8.4 \times 10^{-2}$  mmol) 1,4,8,11-tetramethyl-1,4,8,11-tetraazocyclotetradecane, 1mL 1-butyl alcohol and 20 mL ( $14 \times 10^{-2}$  mmol) diethyl 2-bromo-2-methylmalonate. Two “freeze-pump-thaw” cycles were performed on the contents of the tube to insure that oxygen was removed from the polymerization solution. The tube was sealed under vacuum and placed in an oil bath thermostated at 90 °C. After 6 h the tube were removed from the oil bath and cooled to 0 °C in order to quench the polymerization. Afterwards, the tube was broken, and the contents were dissolved in 10 mL of DMF. Conversion of the monomer was measured using GC, and the molecular weight and polydispersity were measured by GPC. The conversion was 95 %,  $M_n = 21300$ ,  $M_w/M_n = 1.38$ . The  $^1H$  NMR spectrum confirmed that the polymerization involved only the methacrylamide unsaturation of the monomer.

### **Statistical Copolymerizations (Spontaneous Gradient Copolymers)**

#### **Copolymers of Styrene and Acrylonitrile.**

### **Example 101**

6.3 ml ( $5.5 \times 10^{-2}$  mole) of styrene, 3.7 ml ( $5.5 \times 10^{-2}$  mole) of acrylonitrile, 0.1720 g of CuBr, 0.5590 g of 2,2'-bipyridine, 163 l of 1-phenylethyl bromide and 1 g of p-dimethoxybenzene as an internal standard for GC were added to a schlenk flask under argon and the reaction mixture was heated at 80 °C. Samples of the reaction mixture were withdrawn at the prescribed time intervals. The conversion of the monomers was determined by GC and from that the cumulative copolymer composition ( $F_c$ ) was calculated.  $^1H$ -NMR was used to confirm the calculated composition. The molecular weights and molecular weight distributions were determined by Gel Permeation Chromatography vs. polystyrene standards. The results are tabulated below:

Sample	Time (hrs.)	Conversion (%)	$M_n$ (GPC)	$M_w/M_n$	$F_{cAN}$ (GC)	$F_{cAN}$ (NMR)
1	1.5	23	2,000	1.23	0.48	-
2	2.5	67	4,000	1.13	0.50	-
3	3.5	89	7,300	1.08	0.49	-
4	5.5	91	7,800	1.09	0.48	0.48

### Example 102

7.82 ml ( $6.8 \times 10^{-2}$  mole) of styrene, 2.25 ml ( $3.4 \times 10^{-2}$  mole) of acrylonitrile, 0.1720 g of CuBr, 0.5590 g of 2,2'-bipyridine, 163 l of 1-phenylethyl bromide and 1 g of p-dimethoxybenzene as an internal standard for GC were added to a schlenk flask under argon and the reaction mixture was heated at 80 °C. Samples of the reaction mixture were withdrawn at the prescribed time intervals. The conversion of the monomers was determined by GC and from that the cumulative copolymer composition ( $F_c$ ) was calculated.  $^1H$ -NMR was used to confirm the calculated composition. The molecular weights and molecular weight distributions were determined by Gel Permeation Chromatography vs. polystyrene standards. The results are tabulated below:

Sample	Time (hrs.)	Conversion (%)	$M_n$ (GPC)	$M_w/M_n$	$F_{cAN}$ (GC)	$F_{cAN}$ (NMR)
1	1.5	35	1,200	1.35	0.38	-
2	3.5	67	5,400	1.11	0.37	-
3	4.5	89	6,000	1.10	0.33	-
4	5.5	91	6,900	1.09	0.35	0.37

### Example 103

5.0 ml ( $4.4 \times 10^{-2}$  mole) of styrene, 5.0 ml ( $7.6 \times 10^{-2}$  mole) of acrylonitrile, 0.0720 g of CuBr, 0.1560 g of 2,2'-bipyridine, 69 l of 1-phenylethyl bromide and 1 g of p-dimethoxybenzene as an internal standard for GC were added to a schlenk flask under argon and the reaction mixture was

heated at 90 °C. Samples of the reaction mixture were withdrawn at the prescribed time intervals. The conversion of the monomers was determined by GC and from that the cumulative copolymer composition ( $F_c$ ) was calculated. The molecular weights and molecular weight distributions were determined by Gel Permeation Chromatography vs. polystyrene standards. The results are tabulated below:

Sample	Time (hrs.)	Conversion (%)	$M_n$ (GPC)	$M_w/M_n$	$F_{cAN}$ (GC)
1	1.5	12	2,130	1.40	0.46
2	3.3	44	3,600	1.30	0.63
3	18.3	54	7,400	1.10	0.62
4	24.3	60	8,900	1.13	0.62
5	44.3	93	12,100	1.12	0.63

#### Example 104

6.5 ml ( $5.5 \times 10^{-2}$  mole) of styrene, 3.5 ml ( $5.5 \times 10^{-2}$  mole) of acrylonitrile, 0.0172 g of CuBr, 0.1400 g of 4, 4'-di-(5-nonyl)-2,2'-bipyridine, 16.3 l of 1-phenylethyl bromide and 1 g of p-dimethoxybenzene as an internal standard for GC were added to a schlenk flask under argon and the reaction mixture was heated at 90 °C. Samples of the reaction mixture were withdrawn at the prescribed time intervals. The conversion of the monomers was determined by GC and from that the cumulative copolymer composition ( $F_c$ ) was calculated. The molecular weights and molecular weight distributions were determined by Gel Permeation Chromatography vs. polystyrene standards. The results are tabulated below:

Sample	Time (hrs.)	Conversion (%)	$M_n$ (GPC)	$M_w/M_n$	$F_{cAN}$ (GC)
1	2.5	19	8,200	1.31	0.54
2	4.3	25	11,000	1.18	0.42

3	20.0	40	25,800	1.09	0.43
4	27.0	46	27,300	1.08	0.42
5	44.0	52	36,000	1.11	0.42
6	53.0	58	38,900	1.09	0.44

### Copolymers of Styrene and Butyl Acrylate

#### Example 105

7.65 ml ( $6.7 \times 10^{-2}$  mole) of styrene, 6.35 ml ( $4.4 \times 10^{-2}$  mole) of butyl acrylate, 0.0404 g of CuBr, 0.350 g of 4, 4'-di-(5-nonyl)-2,2'-bipyridine, 30 l of methyl 2-bromopropionate and 1 ml of o-xylene as an internal standard for GC were added to a schlenk flask under argon and the reaction mixture was heated at 110 °C. Samples of the reaction mixture were withdrawn at the prescribed time intervals. The conversion of the monomers was determined by GC and from that the cumulative copolymer composition ( $F_c$ ) was calculated.  $^1\text{H-NMR}$  was used to confirm the calculated composition. The molecular weights and molecular weight distributions were determined by Gel Permeation Chromatography vs. polystyrene standards. The results are tabulated below:

sample	time (hrs.)	conversion (%)	$M_n$ (GPC)	$M_w/M_n$	$F_{cBA}$ (GC)	$F_{cBA}$ (NMR)
1	1.25	18	10,800	1.10	0.22	0.24
2	2.75	27	17,600	1.10	0.39	-
3	4.25	49	23,500	1.10	0.32	0.34
4	5.75	56	30,000	1.11	0.43	0.37
5	8.25	68	32,100	1.12	0.35	0.37
6	12.25	72	34,300	1.09	0.35	0.38

#### Example 106

3.39 ml ( $3 \times 10^{-2}$  mole) of styrene, 10.61 ml ( $7.4 \times 10^{-2}$  mole) of butyl acrylate, 0.0404 g of CuBr, 0.350 g of 4, 4'-di-(5-nonyl)-2,2'-bipyridine, 30 l of methyl 2-bromopropionate and 1 ml of o-

xylene as an internal standard for GC were added to a schlenk flask under argon and the reaction mixture was heated at 110 °C. Samples of the reaction mixture were withdrawn at the prescribed time intervals. The conversion of the monomers was determined by GC and from that the cumulative copolymer composition ( $F_c$ ) was calculated. The molecular weights and molecular weight distributions were determined by Gel Permeation Chromatography vs. polystyrene standards. The results are tabulated below:

sample	time (hrs.)	conversion (%)	$M_n$ (GPC)	$M_w/M_n$	$F_{cBA}$ (GC)
1	1	7.9	3,000	1.25	0.53
2	2	15	5,100	1.15	0.54
3	4.5	26	8,800	1.10	0.59
4	11	27	9,300	1.09	0.61
5	14	27	12,000	1.09	0.59

### Example 107

8.33 ml ( $7.3 \times 10^{-2}$  mole) of styrene, 4.62 ml ( $3.2 \times 10^{-2}$  mole) of butyl acrylate, 0.0404 g of CuBr, 0.350 g of 4, 4'-di-(5-nonyl)-2,2'-bipyridine, 30 l of methyl 2-bromopropionate and 1 ml of xylene as an internal standard for GC were added to a schlenk flask under argon and the reaction mixture was heated at 110 °C. Samples of the reaction mixture were withdrawn at the prescribed time intervals. The conversion of the monomers was determined by GC and from that the cumulative copolymer composition ( $F_c$ ) was calculated. The molecular weights and molecular weight distributions were determined by Gel Permeation Chromatography vs. polystyrene standards. The results are tabulated below:

sample	time (hrs.)	conversion (%)	$M_n$ (GPC)	$M_w/M_n$	$F_{cBA}$ (GC)
1	1.00	9.6	3,600	1.29	0.14
2	2.00	15.0	5,300	1.18	0.19
3	4.50	24.0	8,400	1.13	0.17

4	10.5	42.0	16,400	1.12	0.14
5	13.5	76.0	23,700	1.11	0.16

### Copolymers of Isobutene with Acrylonitrile by ATRP.

#### Example 108

##### Alternating copolymers isobutylene/acrylonitrile (molar feed 3.5:1)

To 0.11 g ( $6.68 \times 10^{-4}$  mole) 2,2'-bipyridine and 0.036 g ( $2.34 \times 10^{-4}$  mole) CuBr at -30 °C in a glass tube, was added 1.75 mL ( $2 \times 10^{-2}$  mole) isobutene, 0.5 mL ( $0.55 \times 10^{-2}$  mole) acrylonitrile (AN) and 0.040 mL ( $2.34 \times 10^{-4}$  mole) diethyl methyl bromomalonate under an argon atmosphere. The glass tube was sealed under vacuum and the reaction mixture warmed at 50 °C for 12 hours. The reaction mixture was then dissolved in THF and conversion of AN determined by GC was 100%. The polymer was then precipitated into methanol (three times), filtered, dried at 60 °C under vacuum for 48 h and weighted.  $M_w/M_n=1.45$  ( $M_{th}=3400$ ). The % of acrylonitrile in copolymer determined by integration of methyne proton -CHCN and gem-dimethyl region of  $^1H$ -NMR was 51 %. The glass transition temperature of product determined by DSC was 48 °C.

#### Example 109

##### Copolymer IB/AN (molar feed 1:1)

To 0.055 g ( $3.5 \times 10^{-4}$  mole) 2,2'-bipyridine and 0.017 g ( $1.17 \times 10^{-4}$  mole) CuBr at -30 °C in a glass tube, was added 0.5 mL ( $0.55 \times 10^{-2}$  mole) isobutene, 0.5 mL ( $0.55 \times 10^{-2}$  mole) acrylonitrile and 0.016 mL ( $1.17 \times 10^{-4}$  mole) diethyl methylbromomalonate under an argon atmosphere. The glass tube was sealed under vacuum and the reaction mixture warmed at 50 °C for 24 hours. The reaction mixture was then dissolved in THF and conversion of AN determined by GC was 100 %. The polymer was then precipitated into methanol (three times), filtered, dried at 60°C under vacuum for 48 h and weighted.  $M_n=6400$ ,  $M_w/M_n=1.52$  ( $M_{th}=6500$ ). The % of acrylonitrile in copolymer determined by integration of methine proton -CHCN and gem-dimethyl region of  $^1H$ -NMR was 74 %. The glass transition temperature of product determined by DSC was 70 °C.

## Copolymers of Methyl Acrylate and Vinyl Acetate

### Example 110

**Copolymerization of Methyl Acrylate and Vinyl Acetate by ATRP:** The following amounts of reagents were weighed into a glass tube under ambient temperature: 6.2 mg (0.047 mmol) of CuBr, 21.9 mg (0.140 mmol) of 2,2'-bipyridine. 0.50 ml (5.55 mmol) of methyl acrylate, 0.50 ml (5.42 mmol) of vinyl acetate and 6.1 mL (0.047 mmol) ethyl 2-bromopropionate was added via syringe to the tubes charged with argon. Two “freeze-pump-thaw” cycles were performed on the contents of the tube to insure that oxygen was removed from the polymerization solution. The tubes were sealed under vacuum and placed in an oil bath thermostated at 110 °C. At timed intervals, the tubes were taken from the oil bath and opened. The contents were dissolved in 10 mL of THF. Conversion of the monomers was measured using GC, and the molecular weight and polydispersity were obtained by GPC.

<u>Sample</u>	<u>Time (h)</u>	<u>Conversion (%) of MA</u>	<u>Conversion (%) of VAc</u>	<u><math>M_n</math> Cal</u>	<u><math>M_n</math> SEC</u>	<u><math>M_w / M_n</math></u>
1	0.8	23	5	2780	4190	1.93
2	2.4	52	22	7480	7000	1.47
3	3.3	65	12	7810	9420	1.38
4	4.6	77	26	8940	11100	1.32
5	6.4	87	30	11700	12400	1.28

### Example 111

**Copolymerization of Methyl Acrylate and Vinyl Acetate by ATRP:** The following amounts of reagents were weighed into a glass tube under ambient temperature: 3.98 mg (0.028 mmol) of CuBr, 22.7 mg (0.056 mmol) of 4,4'-di-(5-nonyl)-2,2'-bipyridine. 0.50 ml (5.55 mmol) of methyl acrylate, 0.51 ml (5.55 mmol) of vinyl acetate and 24.6 mL (0.221 mmol) of methyl 2-bromopropionate was added via syringe into the tubes charged with argon. Two “freeze-pump-thaw” cycles were performed on the contents of the tube to insure that oxygen was removed from the polymerization solution. The tube was sealed under vacuum and placed in an oil bath thermostated at 110 °C. After 18.7 hours, the tube was removed from the oil bath and opened.

The contents were dissolved in 10 mL of THF. Conversion of the monomer was measured using GC, and the molecular weight and polydispersity were obtained by GPC. Conversion of methyl acrylate was 58.0%, and conversion of vinyl acetate was 14.0%. The content of vinyl acetate determined by  $^1\text{H}$  NMR was 16.9%.  $M_{th} = 1720$ ,  $M_{n(GPC)} = 1840$ ,  $M_w/M_n = 1.33$

### **Alternating Copolymer of N-Cyclohexyl Maleimide / Styrene**

#### **Example 112**

**General procedure for homogenous ATRP of styrene/N-cyclohexyl maleimide:** The following amounts of reagents were weighed into glass tube under ambient temperature: 12 mg ( $8.37 \times 10^{-2}$  mmol) of CuBr, 0.45 mL (0.41 g, 4.4 mmol) of deinhibited styrene, 0.72 g (4.4 mmol) N-cyclohexyl maleimide, 60 mg (0.175 mmol) 4,4'-di-(5-nonyl)-2,2'-bipyridine, and 12 mL ( $8.8 \times 10^{-2}$  mmol) 1-phenylethyl bromide. Two "freeze-pump-thaw" cycles were performed on the content of tube in order to ensure that oxygen was removed from the polymerization solution. The tube was sealed under vacuum and placed in an oil bath thermostated at 110 °C. After 7 h the tube was broken and the contents dissolved in 10 mL of THF. Conversion of the monomer, measured using GC was 98 % for both monomers, and the molecular weight and polydispersity measured by GPC were  $M_n = 4700$ , and  $M_w/M_n = 1.22$ . From  $^1\text{H}$  NMR spectrum the content of styrene in copolymer was 50 %. DSC measurement showed one  $T_g = 270$  °C. The initial temperature of decomposition of the alternating copolymer determined from TGA was 430 °C.

### **Alternating Isobutylene / Butyl Acrylate**

#### **Example 113**

**Alternating copolymers isobutylene/butyl acrylate (molar feed 3.5:1):** To 0.11 g ( $6.68 \times 10^{-4}$  mole) 2,2' - bipyridine and 0.036 g ( $2.34 \times 10^{-4}$  mole) CuBr at -30 °C in a glass tube, was added 1.75 mL ( $2 \times 10^{-2}$  mole) isobutene, 0.5 mL ( $0.55 \times 10^{-2}$  mole) butyl acrylate (BA) and 0.040 mL ( $2.34 \times 10^{-4}$  mole) diethyl methyl bromomalonate under an argon atmosphere. The glass tube was sealed under vacuum and the reaction mixture warmed to 50 °C for 12 hours. The reaction mixture was then dissolved in THF and the conversion of BA as determined by GC was 100 %. The polymer was then precipitated into methanol (three times), filtered, dried at 60°C under

vacuum for 48 h and weighted.  $M_n=3180$ ,  $M_w/M_n=1.38$  ( $M_{th}=3400$ ). The content of isobutene in the copolymer was determined by integration of  $C(O)OCH_2$  from butyl acrylate and the gem-dimethyl region of the  $^1H$ -NMR spectrum was 49 %. The  $T_g$  of product, as determined by DSC, was -48 °C.

#### **Example 114**

**Copolymer IB/BA (molar feed1:1):** To 0.055 g ( $3.5 \times 10^{-4}$  mole) 2,2' - bipyridine and 0.017 g ( $1.17 \times 10^{-4}$  mole) CuBr at -30°C in a glass tube, were added 0.5 mL ( $0.55 \times 10^{-2}$  mole) isobutene, 0.5 mL ( $0.55 \times 10^{-2}$  mole) butyl acrylate and 0.016 mL ( $1.17 \times 10^{-4}$  mole) diethyl methyl bromomalonate under an argon atmosphere. The glass tube was sealed under vacuum and the reaction mixture warmed to 50 °C for 12 hours. The reaction mixture was then dissolved in THF and the conversion of butyl acrylate, as determined by GC, was 100 %. The polymer was then precipitated into methanol (three times), filtered, dried at 60°C under vacuum for 48 h and weighted. The content of IB in copolymer was 28 % and  $M_n=6400$ ,  $M_w/M_n=1.52$  ( $M_{th}=6500$ ). The % of IB in copolymer was determined from integration of  $C(O)OCH_2$  from butyl acrylate and the gem-dimethyl region of the  $^1H$ -NMR spectrum. The  $T_g$  of the product, as determined by DSC, was -35 °C.

### **Gradient Copolymers**

#### **Styrene / Acrylonitrile**

#### **Example 115**

10 ml of styrene, 0.172 g of CuBr, 0.560 g of 2,2'-bipyridine and 163 l of 1-phenylethyl bromide were added under argon to a three-neck round bottom flask equipped with a condenser and a stir bar. The reaction mixture was heated at 85 °C and the second comonomer, acrylonitrile, was added via an HPLC pump with a rate of addition 0.02 ml/min. Samples of the reaction mixture were withdrawn at the prescribed time intervals. The molecular weights and molecular weight distributions were determined by Gel Permeation Chromatography vs. polystyrene standards. The polymer yield was determined gravimetrically. The cumulative

copolymer composition (Fc) was determined by  $^1\text{H-NMR}$ . Based on the GPC and NMR results, the instantaneous copolymer composition (Fi) was calculated. The results are tabulated below.

sample	time (hrs.)	polymer yield (g)	$M_n$ (GPC)	$M_w/M_n$	$F_{cAN}$ (NMR)	$F_{iAN}$
1	0.5	0.24	1,140	1.45	0.16	0.16
2	2.2	0.33	1,900	1.36	0.19	0.24
3	3.2	1.71	2,470	1.30	0.26	0.42
4	5.2	6.83	5,800	1.12	0.36	0.45
5	6.7	9.91	8,600	1.13	0.39	0.46
6	8.2	12.85	12,300	1.10	0.47	0.62
7	9.7	14.57	15,800	1.10	0.52	0.68

### Example 116

10 ml of styrene, 0.172 g of CuBr, 0.560 g of 2,2'-bipyridine and 163 1 of 1-phenylethyl bromide were added under argon to a three-neck round bottom flask equipped with a condenser and a stir bar. The reaction mixture was heated at 85 °C and the second comonomer, acrylonitrile, was added via an HPLC pump with a rate of addition 0.08 ml/min. Samples of the reaction mixture were withdrawn at the prescribed time intervals. The molecular weights and molecular weight distributions were determined by Gel Permeation Chromatography vs. polystyrene standards. The polymer yield was determined gravimetrically. The cumulative copolymer composition (Fc) was determined by  $^1\text{H-NMR}$ . Based on the GPC and NMR results, the instantaneous copolymer composition (Fi) was calculated. The results are tabulated below.

sample	time (hrs.)	polymer yield (g)	$M_n$ (GPC)	$M_w/M_n$	$F_{cAN}$ (NMR)	$F_{iAN}$
1	1.0	2.00	1,330	1.35	0.36	0.36
2	2.0	3.17	3,400	1.19	0.41	0.44
3	3.0	7.31	5,600	1.11	0.50	0.59
4	4.5	11.84	8,200	1.10	0.53	0.62
5	5.5	13.97	11,900	1.09	0.55	0.69
6	7.5	22.34	17,600	1.10	0.63	0.77
7	9.5	25.54	20,900	1.10	0.71	1.00

### Example 117

10 ml of styrene, 10 ml of diphenyl ether (solvent), 0.172 g of CuBr, 0.560 g of 2,2'-bipyridine, and 163 l of 1-phenylethyl bromide were added under argon to a three-neck round bottom flask equipped with a condenser and a stir bar. The reaction mixture was heated at 90 °C and the second comonomer, acrylonitrile, was added via an HPLC pump with a rate of addition 0.03 ml/min. Samples of the reaction mixture were withdrawn at the prescribed time intervals. The molecular weights and molecular weight distributions were determined by Gel Permeation Chromatography vs. polystyrene standards. The polymer yield was determined gravimetrically. The cumulative copolymer composition (Fc) was determined by <sup>1</sup>H-NMR. Based on the GPC and NMR results, the instantaneous copolymer composition (Fi) was calculated. The results are tabulated below.

sample	time (hrs.)	polymer yield (g)	M <sub>n</sub> (GPC)	M <sub>w</sub> /M <sub>n</sub>	F <sub>cAN</sub> (NMR)	F <sub>IAN</sub>
1	2.0	1.18	3,500	1.15	0.33	0.33
2	3.0	2.89	4,000	1.14	0.34	0.40
3	4.5	6.54	7,700	1.10	0.39	0.44
4	6.5	8.67	9,300	1.09	0.42	0.55
5	8.5	8.89	11,300	1.09	0.45	0.58
6	11.5	9.12	14,000	1.11	0.50	0.68
7	12.5	10.23	15,400	1.11	0.52	0.70
8	15.5	10.73	17,200	1.11	0.55	0.81
9	18.5	13.43	17,400	1.11	0.56	0.82
10	35.0	14.2	18,300	1.16	0.58	0.88

### Example 118

10 ml of acrylonitrile, 10 ml of diphenyl ether (solvent), 0.172 g of CuBr, 0.560 g of 2,2'-bipyridine, and 163 l of 1-phenylethyl bromide were added under argon to a three-neck round bottom flask equipped with a condenser and a stir bar. The reaction mixture was heated at 80 °C and the second comonomer, styrene, was added via an HPLC pump with a rate of addition 0.02 ml/min. Samples of the reaction mixture were withdrawn at the prescribed time intervals. The molecular weights and molecular weight distributions were determined by Gel Permeation Chromatography vs. polystyrene standards. The polymer yield was determined gravimetrically.

The cumulative copolymer composition (Fc) was determined by  $^1\text{H-NMR}$ . Based on the GPC and NMR results, the instantaneous copolymer composition (Fi) was calculated. The results are tabulated below.

sample	time (hrs.)	polymer yield (g)	$M_n$ (GPC)	$M_w/M_n$	$F_{cAN}$ (NMR)
1	1.3	3.36	5,900	1.14	0.71
2	2.3	6.07	6,700	1.10	0.68
3	3.8	6.57	7,500	1.11	0.66
4	5.3	7.04	8,500	1.11	0.64
5	6.8	7.46	8,900	1.12	0.64
6	8.3	7.92	8,800	1.12	0.61
7	9.8	7.81	8,700	1.14	0.60
8	11.3	8.39	8,100	1.14	0.57
9	14.3	8.56	7,900	1.15	0.60

### Styrene / Butyl Acrylate

#### Example 119

10 ml of styrene, 0.063 g of CuBr, 0.205 g of 2,2'-bipyridine and 64 l of ethyl -(2-bromo isobutyrate) were added under argon to a three-neck round bottom flask equipped with a condenser and a stir bar. The reaction mixture was heated at 120 °C and the second comonomer, butyl acrylate, was added via an HPLC pump with a rate of addition 0.02 ml/min (total amount added 25 ml). Samples of the reaction mixture were withdrawn at the prescribed time intervals. The molecular weights and molecular weight distributions were determined by Gel Permeation Chromatography vs. polystyrene standards. The cumulative copolymer composition (Fc) was determined by  $^1\text{H-NMR}$ . Based on the GPC and NMR results, the instantaneous copolymer composition (Fi) was calculated. The results are tabulated below. The final yield of the precipitated and purified polymer, as determined gravimetrically, was 8 g.

sample	time (hrs.)	$M_n$ (GPC)	$M_w/M_n$	$F_{cBA}$ (NMR)	$F_{iBA}$
1	1.0	4,700	1.18	0.17	0.17
2	2.5	9,000	1.18	0.19	0.21

3	3.5	12,400	1.23	0.23	0.34
4	5.0	19,000	1.24	0.29	0.41
5	7.5	27,800	1.41	0.36	0.52
6	11.3	29,000	1.50	0.41	0.65
7	15.0	34,300	1.50	0.46	0.94
8	21.5	45,400	1.59	0.57	0.95

### Example 120

10 ml of styrene, 0.063 g of CuBr, 0.420 g of 4, 4'-di-(5-nonyl)-2,2'-bipyridine and 64 l of ethyl -(2-bromo isobutyrate) were added under argon to a three-neck round bottom flask equipped with a condenser and a stir bar. The reaction mixture was heated at 120 °C and the second comonomer, butyl acrylate, was added via an HPLC pump with a rate of addition 0.08 ml/min (total amount added 13 ml). Samples of the reaction mixture were withdrawn at the prescribed time intervals. The molecular weights and molecular weight distributions were determined by Gel Permeation Chromatography vs. polystyrene standards. The polymer yield was determined gravimetrically. The cumulative copolymer composition (Fc) was determined by <sup>1</sup>H-NMR. Based on the GPC and NMR results, the instantaneous copolymer composition (Fi) was calculated. The results are tabulated below.

sample	time (hrs.)	polymer yield (g)	M <sub>n</sub> (GPC)	M <sub>w</sub> /M <sub>n</sub>	F <sub>cBA</sub> (NMR)	F <sub>iBA</sub>
1	0.9	1.41	3,600	1.17	0.15	0.15
2	2.5	2.51	6,700	1.10	0.20	0.26
3	4.5	3.07	8,900	1.11	0.26	0.49
4	7.5	3.89	11,300	1.13	0.31	0.50
5	9.8	4.18	12,400	1.14	0.32	0.57

### Example 121

10 ml of styrene, 0.063 g of CuBr, 0.420 g of 4, 4'-di-(5-nonyl)-2,2'-bipyridine and 64 l of ethyl -(2-bromo isobutyrate) were added under argon to a three-neck round bottom flask equipped with a condenser and a stir bar. The reaction mixture was heated at 100 °C and the second comonomer, butyl acrylate, was added via an HPLC pump with a rate of addition 0.02 ml/min (total amount added 41 ml). Samples of the reaction mixture were withdrawn at the prescribed time intervals. The molecular weights and molecular weight distributions were determined by Gel

Permeation Chromatography vs. polystyrene standards. The polymer yield was determined gravimetrically. The cumulative copolymer composition ( $F_c$ ) was determined by  $^1\text{H-NMR}$ . Based on the GPC and NMR results, the instantaneous copolymer composition ( $F_i$ ) was calculated. The results are tabulated below.

sample	time (hrs.)	polymer yield (g)	$M_n$ (GPC)	$M_w/M_n$	$F_{cBA}$ (NMR)	$F_{iBA}$
1	4.3	1.57	2,300	1.17	0.06	0.06
2	6.7	3.77	5,100	1.08	0.07	0.08
3	8.5	4.34	6,100	1.08	0.08	0.13
4	10.5	4.97	7,400	1.09	0.10	0.20
5	14.8	5.19	8,100	1.08	0.12	0.34
6	17.8	5.29	9,200	1.08	0.17	0.57
7	20.8	5.41	9,600	1.08	0.18	0.42
8	23.8	5.65	10,400	1.08	0.20	0.44
9	29.8	5.89	10,600	1.08	0.22	0.54
10	33.8	6.01	11,100	1.08	0.29	0.64

### Example 122

**Synthesis of end-functional gradient copolymer:** 10ml of styrene, 0.063g of CuBr, 0.205g of 2,2'-bipyridine and 100 l of functional initiator (glycidyl 2-bromopropionate) were added under argon to a three-neck round bottom flask equipped with a condenser and a stir bar. The reaction mixture was heated at 80°C and the second comonomer, butyl acrylate was added via HPLC pump with a rate of addition 0.05 ml/min (total amount added 36ml). Samples of the reaction mixture were withdrawn at the prescribed time intervals. The molecular weights and molecular weight distributions were determined by Gel Permeation Chromatography vs. polystyrene standards. The cumulative copolymer composition and end-functionality were determined by  $^1\text{H-NMR}$ . Based on the GPC and NMR results, the instantaneous copolymer composition was calculated. The results are tabulated below. The final yield of the precipitated and purified polymer, as determined gravimetrically, was 12g. The epoxy functionality as determined by  $^1\text{H-NMR}$  was 0.91.

sample	time (hrs.)	$M_n$ (GPC)	$M_w/M_n$	$F_{cBA}$ (NMR)	$F_{iBA}$
1	2.5	950	1.34	0.12	0.12

2	5.	1700	1.20	0.18	0.25
3	7.5	3500	1.20	0.24	0.34
4	9	4200	1.21	0.28	0.44
5	12	4800	1.22	0.31	0.56

The final polymer (0.5 g) was dissolved in dry THF (5.0ml) and 1.5 ml of a THF solution of tetrabutyl ammonium fluoride (1M) and 0.4 ml of trimethyl silyl azide were added under argon. The reaction was stirred vigorously for 6.5 hr. The final product was isolated by precipitation into MeOH, purified by repeated precipitation into MeOH and dried at RT under vacuum for 24 hrs. The GPC analysis of the material show unchanged molecular weight and polydispersity. The <sup>1</sup>H-NMR analysis showed that epoxy functionality was preserved entirely. Additionally, FT-IR measurements of the material confirmed that the bromine moiety at the other chain end was replaced with azide group with yield of 73%.

### Example 123

**Synthesis of symmetrical gradient copolymer:** 10ml of styrene, 0.063g of CuBr, 0.205g of 2,2'-bipyridine and 0.3ml of a difunctional initiator (1,2-bis(bromopropionyloxy)ethane) were added under argon to a three-neck round bottom flask equipped with a condenser and a stir bar. The reaction mixture was heated at 80°C and the second comonomer, butyl acrylate was added via HPLC pump with a rate of addition 0.05 ml/min (total amount added 42ml). Samples of the reaction mixture were withdrawn at the prescribed time intervals. The molecular weights and molecular weight distributions were determined by Gel Permeation Chromatography vs. polystyrene standards. The cumulative copolymer composition and two-way growth pattern of the chain were determined by <sup>1</sup>H-NMR. Based on the GPC and NMR results, the instantaneous copolymer composition was calculated. The results are tabulated below. The final yield of the precipitated and purified polymer, as determined gravimetrically, was 20g.

sample	time (hrs.)	M <sub>w</sub> (GPC)	M <sub>w</sub> /M <sub>n</sub>	F <sub>c BA</sub> (NMR)	F <sub>IBA</sub>
1	2.5	1300	1.34	0.20	0.20
2	4.	3500	1.23	0.31	0.45
3	6	6800	1.23	0.40	0.56

4	8	7200	1.21.	0.44	0.61
5	12	9400	1.24	0.48	0.64
6	14	10000	1.25	0.52	0.72

## Graft Copolymers

### PVC Graft Copolymer

#### **Example 124**

To  $0.0500\text{ g}$  ( $1.00 \times 10^{-6}$  mole) poly(vinyl chloride -  $\text{r}$  - vinyl chloroacetate (1%)),  $0.0100\text{ g}$  ( $6.97 \times 10^{-5}$  mole)  $\text{CuBr}$ , and  $0.0570\text{ g}$  ( $1.39 \times 10^{-4}$  mole) 4,4'-di(5-nonyl)-2,2'-bipyridine in glass tube,  $2.0\text{ g}$  ( $4.13 \times 10^{-5}$  mole) styrene was added under argon atmosphere. The glass tube was sealed under vacuum and the reaction mixture was heated at  $110\text{ }^{\circ}\text{C}$  for 12 hours. The reaction mixture was then dissolved in THF and the polymer precipitated into methanol three times. The content of styrene determined by  $^1\text{H NMR}$  was 84 %.  $M_n = 93,600$   $M_w / M_n = 3.11$ .  $T_g = 78.5\text{ }^{\circ}\text{C}$  and  $107.9\text{ }^{\circ}\text{C}$ .

## **Graft Copolymers With Polyethylene Backbones**

#### **Example 125**

**Chlorosulfonated Polyethylene with Styrene Grafts by ATRP:** The following amounts of reagents were weighed into glass tube under ambient temperature:  $0.3\text{ g}$  ( $2 \times 10^{-5}$  mol) chlorosulfonated polyethylene ( $M_n = 14900$ ,  $M_w/M_n = 2.36$ ),  $12\text{ mg}$  ( $8.37 \times 10^{-2}$  mmol) of  $\text{CuBr}$ ,  $1.00\text{ mL}$  ( $0.909\text{ g}$ ,  $8.73\text{ mmol}$ ) of styrene, and  $60\text{ mg}$  ( $0.175\text{ mmol}$ ) 4,4'-di(5-nonyl)-2,2'-bipyridine. Two "freeze-pump-thaw" cycles were performed on the contents of the tube to ensure that oxygen was removed from the polymerization solution. The tube was sealed under vacuum and placed in an oil bath thermostated at  $90\text{ }^{\circ}\text{C}$ . The tube was removed from the oil bath and cooled at  $0\text{ }^{\circ}\text{C}$  in order to quench the polymerization. Afterwards, the tube was broken, and the contents were dissolved in  $10\text{ mL}$  of THF. Conversion of the monomer was measured using GC,

and the molecular weight and polydispersity were measured by GPC. After 24 h, the conversion of styrene was 87 %,  $M_n = 85,600$ ,  $M_w/M_n = 1.79$ .  $^1H$  NMR spectrum shown that graft copolymer contain 70 % styrene.

### **Example 126**

**Chlorosulfonated Polyethylene with Methyl Methacrylate Grafts by ATRP:** The following amounts of reagents were weighed into a glass tube under ambient temperature: 0.3 g ( $2 \times 10^{-3}$  mol) chlorosulfonated polyethylene ( $M_n = 14900$ ,  $M_w/M_n = 2.36$ ), 12 mg ( $8.37 \times 10^{-2}$  mmol) of CuBr, 1.00 mL (0.936 g, 9.36 mmol) of methyl methacrylate, and 60 mg (0.175 mmol) 4,4'-di-(5-nonyl)-2,2'-bipyridine. Two "freeze-pump-thaw" cycles were performed on the contents of the tube to insure that oxygen was removed from the polymerization solution. The tube was sealed under vacuum and placed in an oil bath thermostated at 90 °C. After 8 h, the tube was broken, and the contents were dissolved in 10 mL of THF. Conversion of the monomer was measured using GC, and the molecular weight and polydispersity were measured by GPC. The conversion of methyl methacrylate was 41 %,  $M_n = 26,300$ ,  $M_w/M_n = 1.75$ . The  $^1H$  NMR spectrum showed that the graft copolymer contained 39 % methyl methacrylate.

## **Isobutene Graft Copolymers**

### **Example 127**

**Graft Copolymer of Styrene - Isobutene Elastomer by ATRP** The following amounts of reagents were weighed into glass tubes under ambient temperature: 0.3 g ( $3 \times 10^{-7}$  mol) brominated p-methylstyrene-isobutene elastomer (Exxon) ( $M_n = 108000$ ,  $M_w/M_n = 2.31$ ), 12 mg ( $8.37 \times 10^{-2}$  mmol) of CuBr, 1.00 ml (0.909 g, 8.73 mmol) of styrene, and 60 mg (0.175 mmol) 4,4'-di-(5-nonyl)-2,2'-bipyridine. Two "freeze-pump-thaw" cycles were performed on the contents of the tubes in order to insure that oxygen was removed from the polymerization solution. The tubes were sealed under vacuum and were placed in an oil bath thermostated at 90 °C. At various time intervals the tubes were removed from the oil bath and cooled to 0 °C to quench the polymerization. Afterwards, the tubes were broken, and the contents dissolved in 10 mL of THF.

Conversion of the monomer was measured using GC, and the molecular weight and polydispersity were measured by GPC.

Time (h)	$M_n$ SEC	$M_w/M_n$	mol% St. $^1H$ NMR	$T_g$ , (°C)DSC
0	108000	2.31	-	-60
1	139000	2.48	13.8	-52
1.5	179000	2.55	27.3	0
2	193000	2.59	33.1	5
7	250000	2.38	69	-60/98

### Example 128

**Isobutene - Isobornyl Acrylate Graft Copolymer by ATRP** The following reagents were weighed into a glass tube under ambient temperature: 0.3 g( $3 \times 10^{-7}$  mol) brominated p-methylstyrene-isobutene elastomer (Exxon) ( $M_n = 108380$ ,  $M_w/M_n = 2.31$ ), 12mg ( $8.37 \times 10^{-2}$  mmol) of CuBr, 1.00 mL (0.986 g, 5 mmol) of isobornyl acrylate, and 60 mg (0.175 mmol) 4,4'-di-(5-nonyl)-2,2'-bipyridine. Two "freeze-pump-thaw" cycles were performed on the contents of the tube to insure that oxygen was removed from the polymerization solution. The tube was sealed under vacuum and placed in an oil bath thermostated at 90 °C. After 2 h the tube was removed from the oil bath and cooled to 0 °C to quench the polymerization. Conversion of the monomer was measured using GC; the molecular weight and polydispersity were measured by GPC. Conversion of isobornyl acrylate was 30 %,  $M_n = 141000$ ,  $M_w/M_n = 2.61$ .  $^1H$  NMR spectrum showed that the graft copolymer contained 30 % isobornyl acrylate. By DSC measurement one  $T_g$  was found at 2 °C.

### Butyl Rubber Graft Copolymers

#### Example 129

**Bromo-Butyl Rubber - Styrene Graft Copolymers by ATRP:** The following amounts of reagents were weighed into a glass tube under ambient temperature: 0.3 g( $1.1 \times 10^{-7}$  mol) bromo-butyl rubber (Exxon) ( $M_n = 272500$ ,  $M_w/M_n = 1.78$ ), 12mg ( $8.37 \times 10^{-2}$  mmol) of CuBr, 1.00 mL (0.986 g, 5 mmol) of isobornyl acrylate, and 60 mg (0.175 mmol) 4,4'-di-(5-nonyl)-2,2'-bipyridine. Two "freeze-pump-thaw" cycles were performed on the contents of the tube to insure that oxygen

was removed from the polymerization solution. The tube was sealed under vacuum and placed in an oil bath thermostated at 90 °C. After 2 h the tube was removed from the oil bath and cooled at 0 °C to quench the polymerization. Conversion of the monomer was measured using GC, and the molecular weight and polydispersity were measured by GPC. Conversion of styrene was 21 %,  $M_n = 359000$ ,  $M_w/M_n = 1.72$ .  $^1H$  NMR spectrum showed that the graft copolymer contained 14 % styrene. By DSC measurement one  $T_g$  was found at -51 °C.

### **Example 130**

**Bromo-Butyl Rubber - Isobornyl Acrylate Graft Copolymers by ATRP:** The following amounts of reagents were weighed into a glass tube under ambient temperature: 0.3 g( $1.1 \times 10^{-7}$  mol) bromo-butyl rubber (Exxon) ( $M_n = 272500$ ,  $M_w/M_n = 1.78$ ), 12mg ( $8.37 \times 10^{-2}$  mmol) of CuBr, 1.00 mL (0.909 g, 8.73 mmol) of isobornyl acrylate, and 60 mg (0.175 mmol) 4,4'-di-(5-nonyl)-2,2'-bipyridine. Two "freeze-pump-thaw" cycles were performed on the contents of the tube to insure that oxygen was removed from the polymerization solution. The tube was sealed under vacuum and placed in an oil bath thermostated at 90 °C. After 2 h, the tubes were removed from oil bath and cooled at 0 °C in order to quench the polymerization. Conversion of the monomer was measured using GC, and the molecular weight and polydispersity were determined by GPC. Conversion of isobornyl acrylate was 23 %,  $M_n = 387000$ ,  $M_w/M_n = 1.70$ .  $^1H$  NMR spectrum showed that the graft copolymer contained 18 % isobornyl acrylate. By DSC measurement one  $T_g$  was found at -52 °C.

### **Block Copolymers**

#### **Styrene and Butyl Acrylate**

### **Example 131**

5.0 ml of styrene, 0.0530 g of CuBr, 0.0573 g of 2,2'-bipyridine, 25 l of 1-phenylethyl bromide were added to a schlenk flask under argon and the reaction mixture was heated at 100 °C. The reaction was carried out until the medium solidified. A sample was withdrawn for molecular weight analysis (from Gel Permeation Chromatography:  $M_n = 19,000$  and  $M_w/M_n = 1.15$ ) and the unreacted styrene was removed under vacuum. Then, 10 ml of butyl acrylate and 0.02 g of CuBr

were added under argon and the reaction was allowed to continue at 110 °C for 24 hrs. A sample was again withdrawn from the reaction mixture and analyzed by Gel Permeation Chromatography vs. polystyrene standards giving  $M_n = 28,000$  and  $M_w/M_n = 1.60$ . The copolymer contained 32 % of butyl acrylate as determined by  $^1\text{H-NMR}$ . The overall yield of precipitated copolymer was 50 % (determined gravimetrically).

### **Example 132**

5.0 ml of styrene, 0.0530 g of CuBr, 0.353 g of 4, 4'-di-(5-nonyl)-2,2'-bipyridine, 25 l of 1-phenylethyl bromide were added to a schlenk flask under argon and the reaction mixture was heated at 120 °C. The reaction was carried out until the medium solidified (17 hrs.). A sample was withdrawn for molecular weight analysis (from Gel Permeation Chromatography:  $M_n = 29,000$  and  $M_w/M_n = 1.08$ ) and the unreacted styrene was removed under vacuum. Then, 10 ml of butyl acrylate and 0.02 g of CuBr were added under argon and the reaction was allowed to continue at 100 °C for 24 hrs. A sample was again withdrawn from the reaction mixture and analyzed by Gel Permeation Chromatography vs. polystyrene standards giving  $M_n = 73,000$  and  $M_w/M_n = 1.09$ . The copolymer contained 45 % of butyl acrylate as determined by  $^1\text{H-NMR}$ .

## **Butyl Acrylate and 2 - Hydroxyethyl Acrylate**

### **Example 133**

**Block Copolymerization of Butyl Acrylate with 2-Hydroxyethyl Acrylate by ATRP:** Under an argon atmosphere , 13.3 mL ( $9.3 \times 10^{-2}$  mol) of butyl acrylate was added to 4 g ( $2.5 \times 10^{-2}$  mol) of 2,2'-bipyridine and 1.33 g ( $1.2 \times 10^{-2}$  mol) CuBr in a 50 mL glass flask. The initiator 1.32 mL ( $1.2 \times 10^{-2}$  mol) methyl 2-bromopropionate was then added via syringe. The flask was then immmersed in an oil bath at 90 °C. After 7 h of reaction (the conversion of monomer was 99% and  $M_n = 1100$ ,  $M_w/M_n = 1.45$ ) the second monomer, 6 mL ( $5 \times 10^{-2}$  mol) of 2-hydroxyethyl acrylate was addded. After another 7 h of reaction the flask was cooled to 0 °C to quench the polymerization. Afterwards, the contents of the flask were dissolved in 100 mL of THF. Conversion of the monomer was measured using GC, and the molecular weight and polydispersity

were measured by GPC. The conversion was 97 %,  $M_n = 2,100$ ,  $M_w/M_n = 1.57$ .  $^1\text{H}$  NMR spectrum shown that the copolymer contained 40 % of 2-hydroxyethyl acrylate and 60% butyl acrylate.

## **Block Copolymers with Polynorbornene**

### **Example 134**

#### **Preparation of Polynorbornene Macroinitiator**

The following procedures were done in a glove box: 0.066 g (1.  $2 \times 10^{-4}$  mole)  $\text{Mo}(\text{CHCPhMe}_2)(\text{NAr})(\text{O-t-Bu})_2$  (Ar = 2,6-diisopropylphenyl) in 7ml toluene was placed in a schlenk flask. With stirring, 0.60 g ( $6.37 \times 10^{-3}$  mole) norbornene in 14 ml toluene was added to the flask over 2 min. After stirring for 1.5 hours at room temperature, the reaction was terminated by adding 0.1 g ( $5.02 \times 10^{-4}$  mole) 4-bromomethyl benzaldehyde in 5 ml of toluene. After stirring 1 hour, the reaction mixture was taken from the glove box and mixed with hexane and methanol to precipitate the polymer. The obtained polymer was dissolved in toluene and precipitated into methanol.  $M_n = 12,300$  (GPC),  $M_w/M_n = 1.24$   $T_g = 32^\circ\text{C}$

### **Example 135**

#### **ATRP of Styrene using Polynorbornene as a Macroinitiator**

To 0.100 g (  $1.35 \times 10^{-5}$  mole ) polynorbornene , 5.9 mg ( $4.13 \times 10^{-5}$  mole)  $\text{CuBr}$ , and 0.0338 g ( $4.13 \times 10^{-5}$  mole) 4,4'-di(5-nonyl)-2,2'-bipyridine in a glass tube, 0.43 g ( $4.13 \times 10^{-5}$  mole) styrene was added under an argon atmosphere. The glass tube was sealed under vacuum and the reaction mixture was heated at  $90^\circ\text{C}$  for 19 hours. The reaction mixture was then dissolved in THF and precipitated into methanol three times. The content of styrene determined by NMR was 62 %.  $M_n = 32,100$   $M_w/M_n = 1.16$ ,  $T_g = 45^\circ\text{C}$  and  $95^\circ\text{C}$

### **Example 136**

#### **ATRP of Methyl Acrylate using Polynorbonene as a Macroinitiator**

To 0.050 g (  $6.76 \times 10^{-6}$  mole ) polynorbonene , 7.2 mg ( $5.02 \times 10^{-5}$  mole)  $\text{CuBr}$ , and 0.0408g (  $1.04 \times 10^{-5}$  mole) 4,4'-di(5-nonyl)-2,2'-bipyridine in a glass tube, 0.667 g ( $4.13 \times 10^{-5}$  mole)

methylacrylate and 1.0 ml toluene were added under an argon atmosphere. The glass tube was sealed under vacuum and the reaction mixture heated at 90 °C for 19 hours. The reaction mixture was then dissolved in THF and precipitated into methanol three times. The content of methylacrylate determined by NMR was 37 %.  $M_n = 18,500$ ,  $M_w/M_n = 1.31$ ,  $T_g = 43$  °C and 7 °C.

### **Block Copolymers with Dicyclopentadiene by ATRP**

#### **Example 137**

##### **Preparation of Polydicyclopentadiene macroinitiator**

Following procedures were done in glove box. The Mo-alkylidene complex  $Mo(CHCPhMe_2)(NAr)(O-t-Bu)_2$  (Ar = 2,6-diisopropylphenyl) 0.066g ( $1.2 \times 10^{-4}$  mole) in 7ml toluene was placed in a schlenk flask. With stirring, 0.60g ( $4.54 \times 10^{-3}$  mole) dicyclopentadiene in 14ml toluene was added over 2 min. After stirring 1.5 h at room temperature, the reaction was terminated by adding 0.1 g ( $5.02 \times 10^{-4}$  mole) 4-bromomethyl benzaldehyde in 5 ml of toluene. After stirring an additional hour, the reaction mixture was taken from the glove box. The reaction mixture was mixed with hexane and methanol to precipitate the polymer and the pale yellow precipitate obtained was dissolved in toluene and precipitated again into methanol. Yield of isolated polymer 0.607g (95.1 %).  $M_n$  (NMR) = 7,400 ( $M_{th} = 5,000$ ) and  $M_n$  (GPC) = 12,400,  $M_w / M_n = 1.21$ .  $T_g = 118.9$  °C.

#### **Example 138**

##### **ATRP of Styrene using Polydicyclopentadiene as macroinitiator**

To 0.100 g ( $1.35 \times 10^{-5}$  mole) polydicyclopentadiene, 5.9 mg ( $4.13 \times 10^{-5}$  mole) CuBr, and 0.0338 g ( $4.13 \times 10^{-5}$  mole) 4,4'-di(5-nonyl)-2,2'-bipyridine in a glass tube, 0.43 g ( $4.13 \times 10^{-5}$  mole) styrene was added under an argon atmosphere. The glass tube was sealed under vacuum and the reaction mixture heated at 90°C for 19 hours. The reaction mixture was then dissolved in THF and precipitated into methanol three times. The content of styrene determined by  $^1H$  NMR was 70 %.  $M_n = 20,300$ ,  $M_w / M_n = 1.37$ .  $T_g = 86.4$  °C and 106.9 °C.

### Example 139

#### ATRP of Methyl acrylate using Polydicyclopentadiene as macroinitiator

To 0.050 g ( $6.76 \times 10^{-6}$  mole) polydicyclopentadiene, 7.2 mg ( $5.02 \times 10^{-5}$  mole) CuBr, and 0.0408 g ( $1.04 \times 10^{-5}$  mole) 4,4'-di(5-nonyl)-2,2'-bipyridine in glass tube, 0.667 g ( $4.13 \times 10^{-5}$  mole) methyl acrylate and 1.0 ml toluene were added under argon atmosphere. The glass tube was sealed under vacuum and the reaction mixture was heated at 90°C for 19 hours. The reaction mixture was then dissolved in THF and precipitated into methanol three times. The content of methylacrylate determined by  $^1\text{H}$  NMR was 80 %.  $M_n = 25,600$ ,  $M_w / M_n = 1.48$ .  $T_g = 11.6^\circ\text{C}$  and  $107.0^\circ\text{C}$ .

#### Thermal Properties of ST/BA Copolymers.

Thermal properties of the various ST/BA copolymers were measured via DSC (DSC Plus from Rheometrics). The samples (~ 10 mg) were heated from -100 to 200 °C with a rate 20 °C/ min. The cooling rate was 40°C / min. The second heating was analyzed and the results are reported below:

sample	type	%BA	$M_n$ (MWD)	$T_g$ (°C)
Ex. 105	statistical	34	34,000 (1.10)	20.91
Ex. 119	gradient	57	45,400 (1.59)	0.90
Ex. 121	gradient	24	13,000 (1.08)	-51.84 4.49
Ex. 132	block	45	73,000 (1.15)	-59.99 99.39

## Functionalization of Hyperbranched Polymers

### Example 140

**Preparation of Hyperbranched Polymer with Azide (N<sub>3</sub>) Functional Groups:** Material (0.5 g) as prepared in Example 55, was dissolved in THF (4.0 ml) under dry conditions. Tetrabutyl ammonium fluoride (1.5 ml, 1 M in THF) and trimethylsilyl azide (0.4 ml, 3 mmol) was added via syringe. The exothermic reaction was stirred for six hours. The reaction was quenched by precipitation into MeOH / H<sub>2</sub>O (2X). After drying under vacuum at room temperature, the material was analyzed by IR spectroscopy; a peak at 2115 cm<sup>-1</sup> had formed and was assigned to the azide group. Yield = 80 %. SEC of the azide functional material gave the same molecular weight as the starting material.

## Crosslinked Materials from Hyperbranched Polymers

### Example 141

**Preparation of crosslinked material by heating:** 15.4 mg of polymer obtained from Example 140 was placed in a DSC pan and heated to 250 °C at 20 °C / min using a Rheometrics DSC Plus. A large exotherm was observed with peak temperature, 198 °C, See Figure 1. After cooling the material was removed from the pan and found to be hard and intractible. It was insoluble in THF.

### Example 142

**Preparation of crosslinked material by heating:** Polymer obtained from Example 140 was loaded for simple shear onto a Rheometrics MKIII Dynamic Mechanical Thermal Analyzer and heated to 250 °C at 10 °C / min. At 200 °C. the shear modulus (G') began to increase from 300 Pa until it reached a maximum of 1,000,000 Pa at 220 °C, See Figure 2. After cooling the material was removed from the pan and found to be hard and intractible. It was insoluble in THF.

### Example 143

**Preparation of crosslinked material by irradiation:** 10.0 mg of polymer obtained from Example 140 was placed on a glass slide and irradiated using a mercury lamp. After 6h the material was found to be soft but no longer able to flow. It was insoluble in THF.

### Synthesis of End Functional Polymers

#### Styrene

### Example 144

**Synthesis of End-Functionalized Polystyrene by ATRP:** The following amounts of reagents were weighed into a glass tube under ambient temperature: 6.5 mg ( $4.54 \times 10^{-2}$  mmol) of CuBr, 37.1 mg ( $9.09 \times 10^{-2}$  mmol) 4,4'-di-(5-nonyl)-2,2'-bipyridine, initiator ( $4.54 \times 10^{-2}$  mmol) and 0.50 mL ( $4.54 \times 10^{-1}$  g, 4.35 mmol) of styrene. Three "freeze-pump-thaw" cycles were performed on the contents of the tube to insure that oxygen was removed from the polymerization solution. The tube was sealed under vacuum and placed in an oil bath thermostated at 110 °C. After 3 h the tube was broken, and the contents were dissolved in 5 mL of THF. Conversion of the monomer was measured using GC, and the molecular weight and polydispersity were measured by GPC.

<b>Initiator</b>	<b>Conv. (%)</b>	<b>M<sub>n</sub>, SEC</b>	<b>M<sub>w</sub>/M<sub>n</sub></b>
a-Bromo-p-xylene	51	4400	1.17
a-Bromo-p-tolunitrile	48	5530	1.10
4-Bromobenzylbromide	48	4520	1.16
2-Bromopropionitrile	48	5130	1.09
Bromoacetonitrile	48	4510	1.10

Glycidol			
2-bromopropionate	62	6790	1.12
2-Bromopropionic acid			
tert-butyl ester	41	4030	1.17
Hydroxyethyl			
2-bromopropionate	48	7520	1.10
Vinyl chloroacetate			
	17	1520	1.53
Allyl chloroacetate			
	14	2600	1.77
$\alpha$ -Bromo-n-butyrolactone			
	41	4030	1.17
2-Chloroacetamide	12	4010	1.51

## Methyl Acrylate

### Example 145

**Synthesis of End-Functionalized Poly(Methyl Acrylate) by ATRP:** The following amounts of reagents were weighed into a glass tube under ambient temperature: 6.8 mg ( $4.7 \times 10^{-2}$  mmol) of CuBr, 39.1 mg ( $9.4 \times 10^{-2}$  mmol) 4,4'-di-(5-nonyl)-2,2'-bipyridine, initiator ( $1.2 \times 10^{-1}$  mmol) and 0.50 mL (5.5 mmol) of methyl acrylate. Three "freeze-pump-thaw" cycles were performed on the contents of the tube to insure that oxygen was removed from the polymerization solution. The tube was sealed under vacuum and placed in an oil bath thermostated at 110 °C. After 1.7 h the tube was broken, and the contents were dissolved in 5 mL of THF. Conversion of the monomer was measured using GC, and the molecular weight and polydispersity were measured by GPC.

Initiator	Conv. (%)	M <sub>n</sub> , SEC	M <sub>w</sub> /M <sub>n</sub>
Allyl bromide	49	3420	1.24
2-Bromopropionic acid tert-butyl ester	94	4680	1.22
Hydroxyethyl 2-bromopropionate	97	6830	1.30
$\alpha$ -Bromo-n-butyrolactone	83	4770	1.13

### Multifunctional Initiators

#### **1,2-bis(bromopropionyloxy)ethane)**

##### **Example 146**

**Synthesis of 1,2-bis(bromopropionyloxy)ethane:** A 500 ml schlenk flask containing a 3/4 inch stir bar was flame dried under argon and charged with 10 ml (0.18 mol) of ethylene glycol, 28 ml (0.20 mol) of triethylamine and 50 ml of diethyl ether. The flask was fitted with a reflux condenser and purged constantly with argon. The apparatus was submerged into an ice/water bath to maintain a 0°C reaction temperature. Dropwise addition of 47 ml (0.45 mol) of bromopropionyl bromide to the reaction solution proceeded. At completion of the reaction, the reaction mixture was filtered to remove insoluble salts. The organic product was separated from byproducts and unreacted starting materials by three 50 ml extractions from an aqueous saturated sodium bicarbonate solution followed by three 50 ml extractions from deionized water. The organic liquid was dried over magnesium sulfate and filtered. The solvent was removed by evaporation. Final purification of the product was achieved by vacuum distillation at 82 - 86°C, 2 mm Hg. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 4.40 (s, 4H), 4.35 (q, 1H), 1.81 (d, 3H). IR (polyethylene film): 3500, 3000, 2950, 2900, 1700, 1460, 1400, 1350, 1290-1230, 1170, 1080 cm<sup>-1</sup>.

### Example 147

**Bulk Polymerization of n-Butyl Acrylate (Initiator = 1,2-bis(bromopropionyloxy)ethane):** A dry round-bottomed flask was charged with CuBr (50.8 mg; 0.349 mmol) and 2,2'-bipyridyl (163.5 mg; 1.05 mmol). The flask was sealed with a rubber septum and was cycled between vacuum and argon three times to remove the oxygen. Degassed *n*-butyl acrylate (28.6 ml; 199.5 mmol) was added using degassed syringes and stainless steel needles. The 1,2-bis(bromopropionyloxy)ethane (1.0 ml; 5 mmol) was added and the flask was immersed in an oil bath held by a thermostat at 80 °C. After stirring overnight, the conversion was 95%, and the produced poly(*n*-butyl acrylate) had  $M_n = 5070$  ( $M_n, th = 5,100$ ) and  $M_w/M_n = 1.28$ .

### Hexakis(4-(2-methylbromopropionyloxy)phenoxy)cyclotriphosphazene

### Example 148

**Synthesis of Hexakis(4-(2-bromopropionyloxy)-phenoxy)cyclotriphosphazene:** Hexakis(4-hydroxymethylphenoxy)cyclotriphosphazene was prepared according to the method of Chang et al. (Chang, J. Y., Ji, H. J.; Han, M. J.; Rhee, S. B.; Cheong, S.; Yoon, M. *Macromolecules* 1994, 27, 1376.) 1.7 g ( $2.0 \times 10^{-3}$  mol) of hexakis(4-hydroxymethylphenoxy)-cyclotriphosphazene was placed into a 100 ml three neck flask containing a 3/4 inch stir bar. The flask, flushed continuously with argon, was fitted with a 50 ml addition funnel and reflux condenser. The apparatus was then charged with 60 ml of diethyl ether and 1.8 ml ( $1.3 \times 10^{-2}$  mol) of triethylamine. The solution was cooled to 0°C in an ice/water bath. A solution of 10 ml diethyl ether and 1.4 ml ( $1.3 \times 10^{-2}$  mol) bromopropionyl bromide was placed into the addition funnel. This solution was added dropwise to the cyclotriphosphazene solution at a rate of 1 drop every 3 seconds. When addition of the bromopropionyl bromide solution was complete, the reaction mixture was allowed to warm to room temperature overnight. The reaction mixture was filtered and washed with diethyl ether. Unreacted acid and soluble salts were separated from the product by three 75 ml extractions into an aqueous solution of saturated sodium bicarbonate followed by two 30 ml extractions into deionized water. The organic phase was dried over magnesium sulfate and the solvent removed by evaporation. The product yellow oil was purified by two separations from cold methanol. Yield = 18%.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $d = 7.2$  (d, 2H), 6.9 (d, 2H), 5.2 (q, 2H),

4.4 (q, 1H), 1.8 (d, 3H). IR (polyethylene film): 3500, 3050, 2980, 1750, 1610, 1500, 1440, 1400, 1360, 1290, 1220-1150  $\text{cm}^{-1}$ .

### Example 149

**Bulk Polymerization of n-Butyl Acrylate (Initiator = hexakis(4-(2-methylbromopropionyloxy)phenoxy)cyclotriphosphazene):** A dry round-bottomed schlenk flask was charged with CuBr (15.0 mg, 0.10 mmol) and 4,4'-di(5-nonyl)-2,2'-bipyridine (85.4 mg, 0.21 mmol). The flask was sealed with a rubber septum and held under vacuum for 20 minutes to remove oxygen. Degassed *n*-butyl acrylate (23.3 ml, 0.16 mol) was then added to the flask under an argon atmosphere using degassed syringes and stainless steel needles. The homogeneous solution was infused with 0.20 ml of a 0.17 M hexakis(4-(2-methylbromopropionyloxy)phenoxy)cyclotriphosphazene ( $3.5 \times 10^{-5}$  mol) solution in benzene. The solution was degassed by sparging with argon for 20 minutes. The septum was replaced with a glass stopper and the flask immersed in an oil bath held by a thermostat at 90 °C. At timed intervals, the glass stopper was substituted for a rubber septum and two samples were withdrawn from the flask using a degassed syringe. One sample was added to deuterated chloroform for conversion measurements by NMR while the other was dissolved in THF for molecular weight determination by SEC.

Sample	Time (h)	Conversion (%)	M <sub>n</sub> , th.	M <sub>n</sub> , SEC	M <sub>w</sub> / M <sub>n</sub>
1	0	0	1,700	1,200	1.05
2	0.3	0	1,700	7,300	1.54
3	0.8	3.4	20,400	8,400	1.70
4	1.8	4.3	25,900	9,500	2.04
5	3.8	8.1	48,700	24,600	1.40
6	8.4	16.8	101,000	45,900	1.67
7	13.9	31.8	191,000	57,400	2.37

These examples provide ample proof that the effect of the present method is wide-ranging and is believed to adequately support the full breadth of the claims in the present application.

4. The undersigned petitioner declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

5. FURTHER DEPONENT SAITH NOT.

Respectfully submitted,

6-13-97

Date

One copy of deposit pending